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THERMAL STABILITY OF HYDROCARBON FUELS

FIRST YEAR SUMMARY TECHNICAL REPORT

AIR FORCE CONTRACT AF 33 (616) - 7241

MAY, 1961

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PHILLIPS PETROLEUM COMPANY

THERMAL STABILITY OF HYDROCARBON FUELS

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Rex Ratchford

Phillips Petroleum Company

JULY 1961

AERONAUTICAL SYSTEMS DIVISION

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July 1961

Aeronautical Systems Division
Air Force Systems Command
United States Air Force
Wright-Patterson Air Force Base, Ohio

FOREWORD

ABSTRACT

Work under Contract AF 33(616)-7241 has two objectives, (1) to develop a small scale jet fuel thermal stability tester capable of operation at fuel temperatures from 300 to 650 F with samples 1 quart or less in size and (2) to study the effects of storage on thermal stability performance of JP-6 grade jet fuels and establish causes (in terms of environmental factors and fuel composition) for any adverse results observed.

The first year of work on thermal stability test methods produced three potentially useful techniques, (1) a recirculating-flow dynamic method measuring deposit insulating effects around a heated surface which requires 1000 ml fuel samples, (2) a static method measuring deposit insulating effects around a heated nickel wire which requires 150 ml fuel samples and (3) a static method based on changes in fuel light transmission characteristics after heating which requires only 5 ml fuel samples. The latter two of these methods will be investigated further.

The results through one year on the JP-6 storage stability investigation showed that three out of five test fuels did deteriorate significantly after 26 weeks at 110 F in terms of CFR Fuel Coker rating, while a fourth fuel showed evidence of deterioration in one container only which is attributed to solids contamination. Vented versus sealed-under-nitrogen storage had no influence on the changes. The only chemical or physical changes in the test fuels after storage which matched the thermal stability changes were the UV light transmission characteristics. The two fuels least affected by storage were low in both sulfur and polycyclic aromatics content. Several phenol type antioxidant additives appeared capable of stabilizing a fuel of poor thermal stability performance when fresh and of maintaining this stability throughout storage, whereas a single amine type additive tested had negative effects on storage stability.

Aromatic nucleus compounds added in small amounts to a stable paraffinic base fuel caused appreciable degradation in thermal stability only when oxidized states (hydroxyl or carbonyl) were present. The influence of oxygen availability on this problem was demonstrated by large increases in fuel peroxide content after thermal stability testing and by improved thermal stability ratings when dissolved air was removed as effectively as possible.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

Marc P. Dunnam

Marc P. Dunnam
Chief, Fuels & Lubricants Branch
Nonmetallic Materials Laboratory
Directorate of Materials and
Processes

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I. INTRODUCTION

The work described in the following report was carried out by Phillips Petroleum Company during the one year period extending from May 1, 1960 through April 30, 1961. Two separate projects were initiated, (1) development of a small sample jet fuel thermal stability test and (2) study of deterioration of JP-6 jet fuel thermal stability performance during storage.

The goals of the test method development project are to ascertain the feasibility of a relatively simple test for evaluating jet fuel thermal stability quality which can be performed with fuel samples less than one quart in size and which will separate fuels in the proper order of quality with respect to both subsonic (300°F) and supersonic (to 650°F) aircraft fuel systems. Work carried out during the period covered by the present report included test methods based on both static and recirculating-flow environments for the heated fuel.

Objectives of the storage stability project are to examine the deterioration in thermal stability quality of a group of JP-6 type jet fuels during controlled storage at both 110 F hot room and ambient temperature conditions and to relate these changes to fuel composition, oxygen availability and the presence of anti-oxidant fuel additives. Performance of the test fuels in this respect is based on CFR Fuel Coker tests, gum content and color, while a wide variety of chemical analyses are being made to isolate the causes for the performance changes observed. This information will ultimately be applied to the recommendation of methods for handling, additive-treating or processing jet fuels to prevent thermal stability performance deterioration during extended periods of storage prior to use.

Both projects are to be continued for a second one-year period under a supplemental agreement to Contract AF 33(616)-7241, so that the present report covering the first year of work only has been termed "First Year Summary Technical Report". Previous reports issued under this contract include Progress Reports No. 1[1] and 2[2], covering the first and second four-month working periods respectively.

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II. SMALL SCALE JET FUEL THERMAL STABILITY TEST METHODS

Jet fuel thermal stability quality is presently controlled in the various military specifications by the CFR Fuel Coker test, using varying temperature conditions to match the differences in thermal severity represented by different classes of military aircraft. Among the well-recognized deficiencies of this test for both research and quality control purposes are the relatively large sample size (6 gallons), lengthy test time (6-7 hours) and high cost ($70-$100) for a single determination. Moreover, the significance of this test appears doubtful with respect to at least one application for JP-6 grade jet fuel, as tested at temperatures between 400 and 450 F, while the apparatus itself is not readily adaptable to temperatures above 450 F.

Therefore the present work has the objective of determining the feasibility of a method for laboratory evaluation of jet fuel thermal stability characteristics which satisfies the following criteria:

(1) Requires less than one quart of test fuel.

(2) Capable of fuel temperatures from 300 to 650 F.

(3) Aligns fuels in proper order of quality for subsonic aircraft in which fuel is heated to 300 or 400 F and for supersonic aircraft in which fuel may be heated well above 450 F.

Base line thermal stability ratings to guide the investigation of suitable small sample test methods will consist of CFR Fuel Coker ratings at fuel temperatures between 300 and 400 F, which will be considered to represent the requirements of present subsonic-transonic military aircraft. For the requirements of Mach-three-plus aircraft the guiding premises will be ratings by another Air Force contractor using both a High Temperature Research Fuel Coker and a special fuel system simulator rig. The fuels are to be provided to Phillips by arrangement with WADD.

As to types of test apparatus, both static and flowing types of systems have been considered. The former offers the potential advantages of far greater simplicity and adaptability to very small fuel samples while the latter approaches more realistically the type of environment in which fuel thermal instability shows itself in jet powerplants.

A. Flowing Fuel Systems

Existing test procedures concerned with jet fuel thermal stability effects have concentrated on measurement of the flow restricting effects and color of the deposits produced. However, it is now understood that a primary undesirable aspect of fuel instability products laid lown as deposits in the fuel side of engine lube oil coolers is loss in heat transfer - which allows lube oil temperatures to rise to undesirably high levels. Therefore it appeared that the possibility of a test

method based on direct measurement of the insulating effects of deposits produced by fuel instability might be profitably followed up under the present contract. This section of the report describes the assembly and testing of a "bread-board" model dynamic or flowing system for the measurement of jet fuel thermal stability in terms of losses in heat transfer coefficient resulting from deposit laydown.

1. Preliminary Design Considerations.

Determination of heat transfer coefficient requires precise indication of the temperature differential across the fluid (and deposit) boundary layer film adjacent to the surface from which heat is being transferred, plus knowledge of the rate of heat flux through this film. Therefore primary considerations in the assembly of a system measuring deposit effects under conditions where forced convection is the controlling mode of heat transfer, are the methods for accurately and repeatably measuring this film Δt and heat input rate. As to the latter, the obvious approach is to employ electrical resistance heating, which enables direct measurement of heat input in terms of wattage. One simple heat transfer system of inherently low heat capacity which has been employed by other investigators[1] concerned with use of fuels as coolant is direct resistance heating of a stainless steel tube around which fuel is flowing and within which thermocouples can be placed for indication of internal surface temperature.

Because of the obvious difficulty, in practical systems, of evaluating the true temperature differential across a fluid film adherent to a heat transfer surface, it is common practice in heat transfer work to express this differential as the difference in temperature between the surface from which heat is being transferred and the average temperature of the main body of the fluid being heated. This premise has been adopted in the present work. Thus, with measurements of tube wall surface temperature, average fuel stream temperature and heat flow rate available, the heat transfer coefficient (or film conductance) in a forced convection system may be calculated from the equation:

$$h_c = \frac{q}{A(T_T - T_F)} \qquad (1)$$

Where: h_c = film conductance (Btu/hr ft^2 $^\circ$F)

q = heat flow rate (Btu/hr.)

A = heat transfer surface area (ft.^{2})

T_T = tube outside surface temperature ($^\circ$F)

T_F = average fuel stream temperature ($^\circ$F)

The foregoing considerations seemed to indicate that a miniature tube and shell heat exchanger utilizing direct resistance electrical heating of the tube and temperature sensing by axially placed thermocouples in the tube offered the most desirable features for the present purposes.

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Figure 1 shows schematically the apparatus put together to investigate this type of approach to evaluating jet fuel thermal instability effects. The proportions of the heat exchanger represent compromises between (1) adequate residence time to achieve fuel-out temperatures as high as 650°F with a maximum electrical heating load of 1 KW, (2) minimum shell diameter to maximize velocity (or Reynolds No.) and (3) adequate clearance between shell and heating tube to avoid electrical short circuiting. Recirculating flow was employed in order to collect sufficient deposit from one liter fuel samples to produce measurable effects on heat transfer. This also allowed independent control of system pressure by admitting nitrogen into the vapor space in the fuel reservoir without requiring any high-pressure-drop devices such as orifices or valves which would be subject to erratic plugging by deposits. It is recognized that the use of recirculating flow does involve some compromises with realism with respect to actual aircraft engine fuel systems.

Metering the rate of fuel flow was achieved by controlling the rpm of the constant displacement gear pump used to recirculate the fuel - thus the pump itself was calibrated to serve as a volumetric flowmeter. Since fuel is usually metered volumetrically in aircraft fuel systems it seemed appropriate to meter the fuel volumetrically in the test apparatus as well. The intercooler shown seemed to reduce the temperature of the fuel stream leaving the heating section to a level which could be withstood by the seals in the gear pump.

Initially metal-sheathed "Ceramo" thermocouples were employed for indication of metal temperatures in the essentially black-body equilibrium radiation environment provided by the interior of the heating tube. However, it soon became apparant that the thermocouple sheaths were short circuiting portions of the applied heating current through the junctions, causing erroneous readings. Thus, fiber glass fabric insulated thermocouples were substituted and were used for all of the tests to be shown in the present report.

Summarized below are a number of the more important design features of the apparatus depicted in Figure 1:

Heat Exchanger – Tube and shell – 1/8" o.d. 304 stainless steel electrically heated tube (.031" wall, 7" heated length) within 1/4" i.d. shell. Tube ends sealed and electrically insulated with 1/4" i.d. x 3/8" o.d. rubberized asbestos ferrules.

Temperature Measurements – Tube wall temperatures – Axial probe from each end, fiber glass insulated i.c. thermocouples.

Fuel temperatures – Radial and/or axial i.c. thermocouple probes at points immediately adjacent to the main heat exchange chamber.
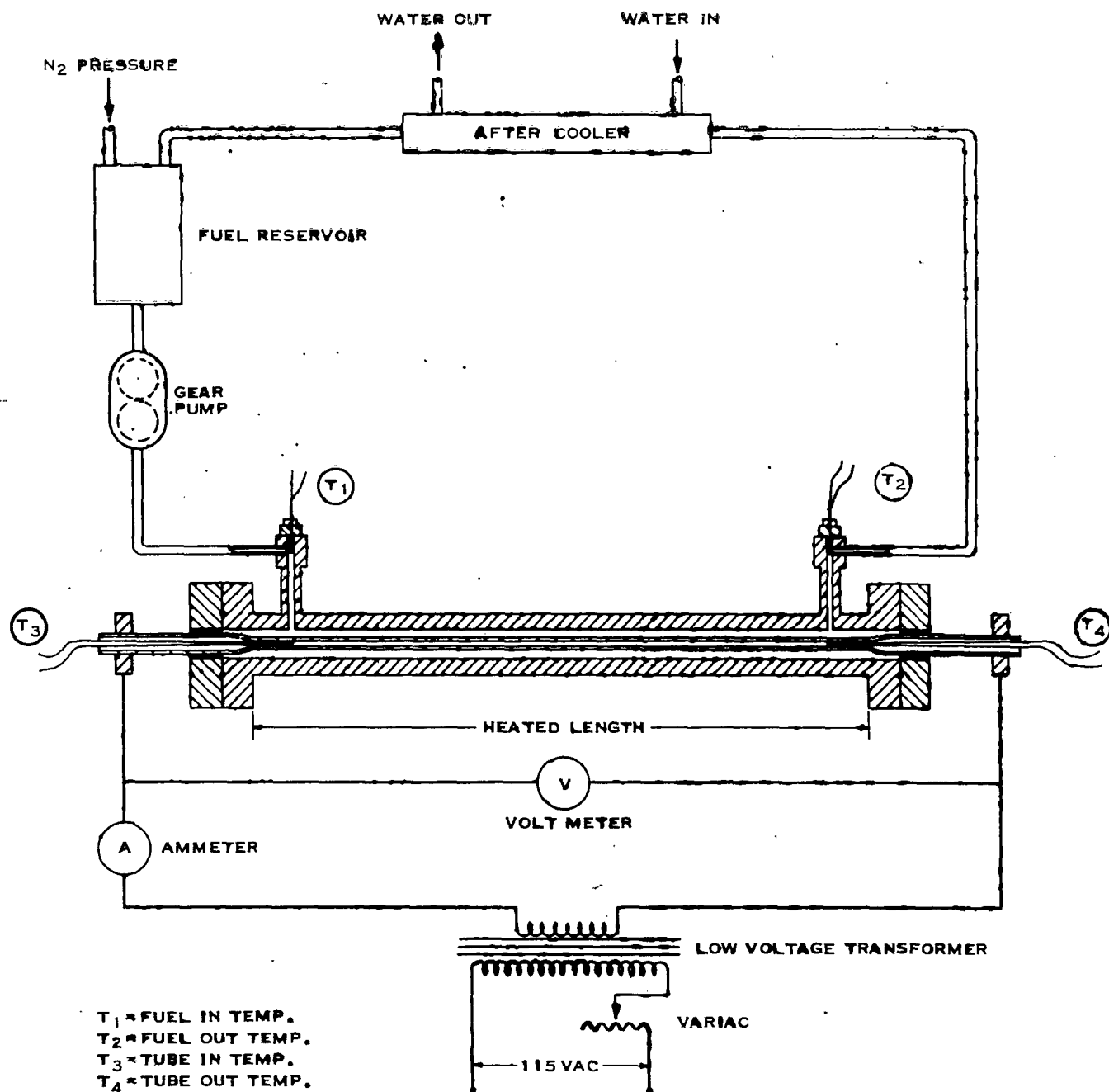
FIGURE 1
SMALL SCALE RECIRCULATING FLOW JET FUEL THERMAL STABILITY TESTER

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<u>Heat Input Source and Control</u> – Source – 10 volt, 1 KVA step-down transformer
(115 v. pri.)

Control – Autotransformer used to vary primary
voltage.

Metering – Voltmeter and ammeter in transform-
er secondary circuit.

<u>Fuel Flow Metering</u> – Eastern Industries Model 1201 gear pump driven by induction
motor through variable speed cone drive.

The test procedure employed consisted of charging one liter of test fuel into
the pre-cleaned apparatus, pressurizing it with nitrogen to 240 psig (dictated by
the pressure rating of the fuel reservoir), adjusting rate of fuel flow to one
gallon per hour and setting the desired level of wattage input. Fuel and tube
temperatures were then monitored at five minute intervals for a total test period
usually two hours in length. The temperature and wattage measurements were then
converted to heat transfer coefficient (h_c) values using the equation shown on
page 3. Most of the testing carried out with this apparatus employed rather
severe heating flux conditions, corresponding to 571 Btu/in^2 of heating surface,
in order to produce measurable fouling effects in reasonably short test durations.

2. Test Results Using JP-Fuels

Table I presents a condensed summary of data obtained with various fuels
following one full hour of operation, which can be considered to represent fully
warmed up conditions. Figure 2 presents complete h_c versus time curves for two
fuels selected for preliminary test work because of known wide differences in
thermal stability quality based on the CFR Fuel Coker test. The isoparaffinic
JP-5 boiling range alkylate fuel produces CFR Fuel Coker heater deposits rating
no heavier than "0" or "1" at 400 F-plus temperature compared with "4" or
heavier ratings for the aged West Coast (JP-5) kerosine. The heat transfer
coefficient data shown in Figure 3 align these two fuels in the same order of
quality as the CFR Fuel Coker preheater ratings, that is the severe heat exchanger
fouling caused by the West Coast kerosine fuel produces peak h_c values falling
25 to 30 units below those for the clean isoparaffinic fuel. Exploratory tests
of varying duration showed that appreciable deposits were laid down by the poorer
of these two fuels as early as ten minutes in the test cycle – well below the time
required for warmup of the apparatus itself. Thus, the peaks shown in the curves
of Figure 2 at about 50-60 minutes running time correspond to equilibrium temp-
erature conditions for an already-fouled heating tube – suggesting that a thermal
stability quality rating can be based on either peak "h_c", or "h_c" level at some
fixed time period after the apparatus is fully warmed up ($>$ 50 minutes).

The next step was to follow up the preliminary indications that this
technique could tell the difference between fuels representing extremes in temp-
erature stability characteristics, using other test fuels varying in CFR Fuel
Coker rating only within the limits allowed by the JP-6 fuel specifications.
Figure 3 shows h_c versus time curves obtained with 6 different JP-6 type fuels
available from the storage stability phase of this contract program. Again
a wide separation in fuel heat transfer performance in this apparatus was shown.

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TABLE I

HEAT TRANSFER DATA OBTAINED WITH THE SMALL SCALE DYNAMIC THERMAL STABILITY TESTER

Dimensions — 1/4" Dia. x 7" Heat Exchanger with 1/8" Dia. Heated Tube.
Pressure — 240 psig
Fuel Flow Rate — 1 GPH with 1 Liter Fuel Charge
Power Input — 390 Watts
Ambient Temperature — 81 F ($\pm$ 6)
Note: Data Below Taken After One Hour's Operating Time

Run	Fuel	Fuel Temperature, °F			Tube Temperature, °F			h_c Btu/Hr. Ft² °F
		In	Out	Avg.	In	Out	Avg.	
23	Isopar _nic Alkylate Fraction (B829)	128	425	277	580	658	619	201
24	Aged West Coast Kerosene (G593D)	126	432	279	630	708	669	177
25	Wright Field F-60-3 (K27)	124	428	276	593	686	640	189
26	West Texas Kerosine + Alkylate (K500)	129	431	280	668	837	753	146
27	West Texas Kerosine + Alkylate (K30)	117	411	264	601	736	669	170
28	Wright Field F-60-5 (K26)	115	407	261	540	625	583	214
29	Midcontinent Kerosine + Alkylate (K28)	121	408	265	565	648	607	201
30	Gulf Coast Kerosine + Alkylate (K29)	113	400	257	560	672	616	192
31	Wright Field F-60-3 (K27)	112	419	266	592	668	630	189
	Power Input — 285 Watts							
36	IBP - 360 F Cut from W.T. Kero.+ Alk.	103	297	200	440	523	482	181
37	360-400 F Cut From W.T. Kero.+ Alk.	107	309	208	473	542	508	170
38	400 F - EP Cut From W.T. Kero.+ Alk.	105	296	201	527	708	618	122

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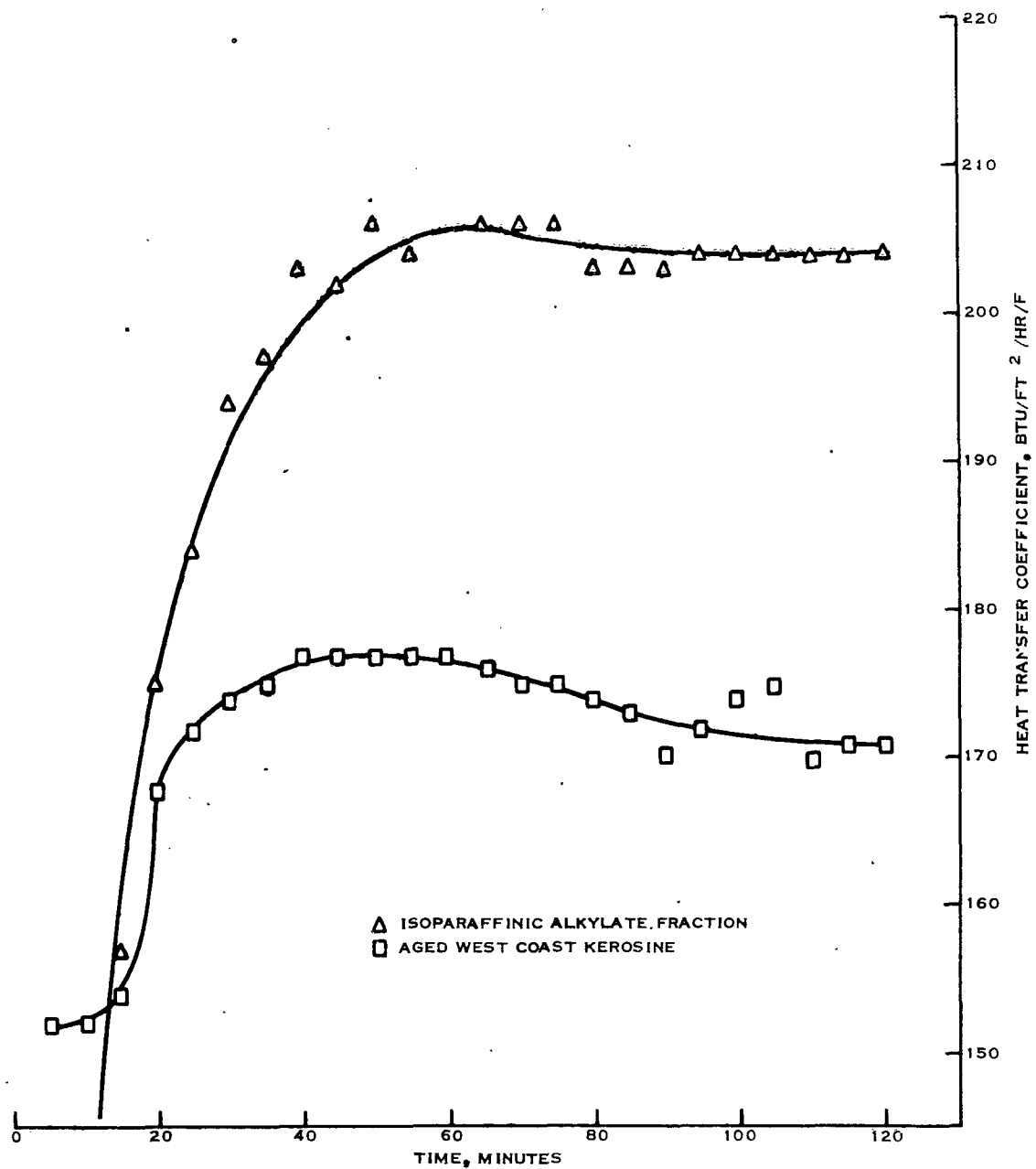
NOTE: FUEL OUTLET TEMP = 420F
. FIBER-GLASS SHEATHED THERMOCOUPLES

FIGURE 2
HEAT TRANSFER PERFORMANCE OF TWO FUELS IN THE
SMALL SCALE RECIRCULATING FLOW JET FUEL THERMAL STABILITY TESTER

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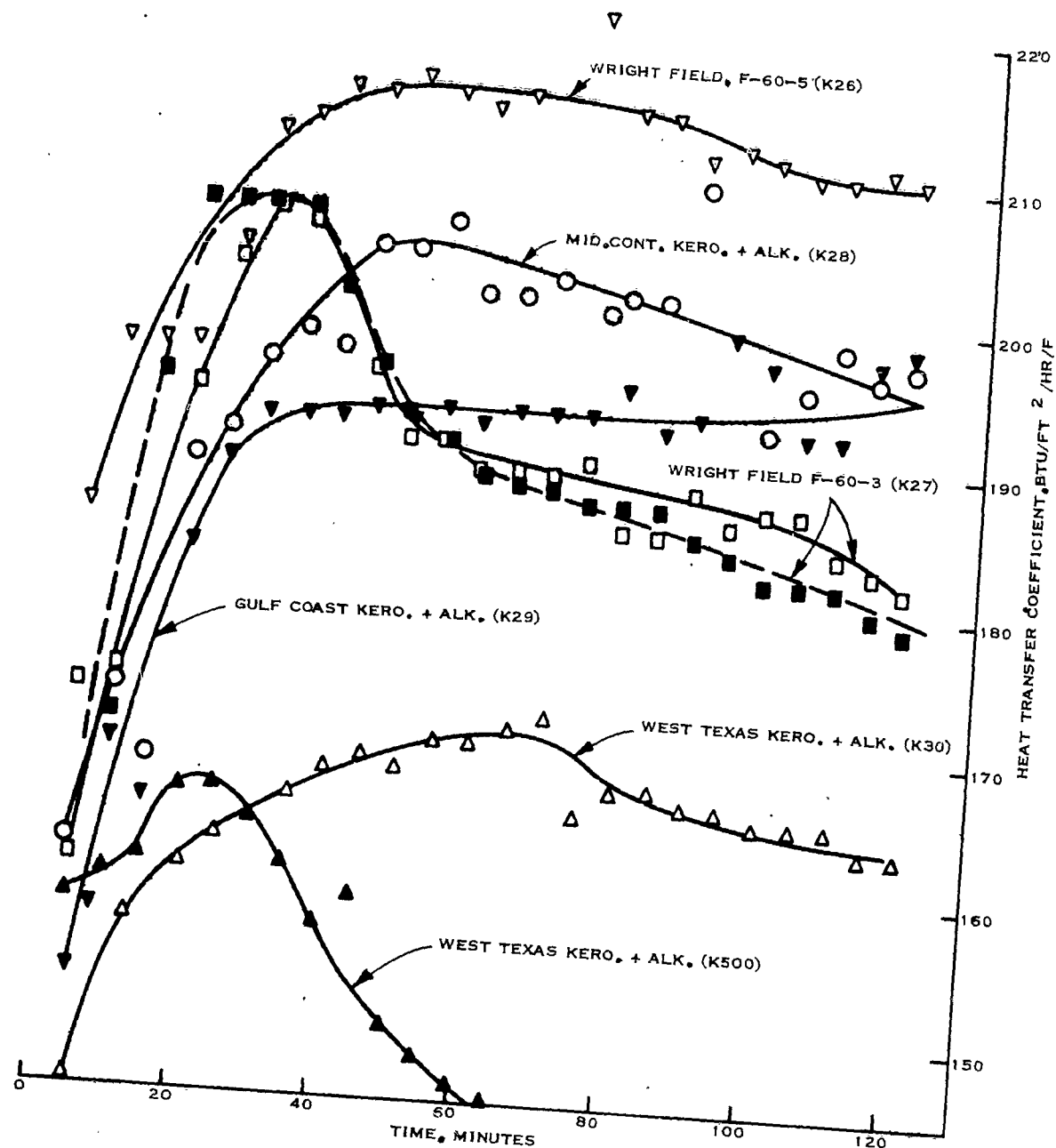
NOTE: FUEL OUTLET TEMP. = 410 TO 420F
FIBER-GLASS SHEATHED THERMOCOUPLES

FIGURE 3
HEAT TRANSFER PERFORMANCE OF JP-6 FUELS IN THE SMALL SCALE
RECIRCULATING JET FUEL THERMAL STABILITY TESTER

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With these, as with the JP-5 type fuels, the apparatus appeared to have detected variations in the rate of build-up of deposits and variations in the thermal resistance of these deposits. In two cases, the K-27 and K-500 runs, the curves dropped off significantly after reaching their peaks, indicating that deposition continued to occur through the duration of these tests and that this dep.. ition was of a type which decreased heat transfer performance. For the balance of the tests the depositing rate appeared to be relatively slow early in the tests and, in general, upon reaching a peak, either very little further deposition occurred or, if any did occur it was not of a type which affected heat transfer performance greatly. At any rate, these data confirmed that the test rig was able to separate fuels on a heat transfer basis. Additionally, these data tell a great deal more about the performance of a fuel than a simple terminal color rating. For example, the deposits produced by fuel K27 were relatively light gray-brown in color, yet the performance of this fuel throughout the last hour of the test was considerably poorer than several of the other fuels whose deposits were considerably blacker.

In order to be assured that the variations in heat transfer coefficient were the result of heat exchanger fouling and not simply those accompanying variations in the physical properties of the fuels, it was decided to consider the effect of these fuel variables on the Nusselt expression:

$$(\text{Nusselt No.}) \approx (\text{Reynolds No.})^{b} \ (\text{Prandtl No.})^{d}$$

In general, the empirically derived modifications of this equation are of the form:

$$Nu \approx (R_e)^{0.8}(P_r)^{0.4} \quad \text{or} \quad \frac{h_c D}{k} \approx \left(\frac{DV}{\gamma}\right)^{0.8} \left(\frac{\rho C_p \gamma}{k}\right)^{0.4}$$

where:
- h_c = Heat transfer coefficient
- D = Characteristic dimension of the heat exchanger
- V = Fluid velocity
- k = Fluid thermal conductivity
- ρ = Fluid density
- γ = Fluid kinematic viscosity
- C_p = Fluid specific heat

By rearranging this proportionality in terms of the effect of fuel properties alone it becomes:

$$h_c \approx k^{0.6} \ \gamma^{-0.4} C_p^{0.4} \ \rho^{0.4}$$

In the absence of actual measurements of C_p estimates of specific heat were obtained for the six JP-6 fuels from the charts of Hougen and Watson (4) using volumetric average boiling points and API gravities for the average fuel temperature attained during each test. Estimates of thermal conductivities were obtained from the nomograph developed by Mapstone (5) based on API gravity, again at average fuel temperatures. Kinematic viscosities were extrapolated to the average fuel temperatures from a plot of the 100 F and 210 F viscosities versus temperature. Density was established from the API gravity of each fuel and then corrected to the test temperatures by using the curves in (6). Substitution of these estimates of K, γ, C_p and ρ into the above proportionality yielded the following:

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Fuel No.	$k^{0.6} \gamma^{-0.4} C_p^{0.4} \rho^{0.4}$
BJ60-10-K26	3.82
BJ60-10-K27	4.04
BJ60-10-K28	3.78
BJ60-10-K29	3.71
BJ60-10-K30	3.73
BJ60-10-K500	3.76

Thus, the large variations in heat transfer coefficients observed in the tests cannot be attributed simply to variations in the physical properties of the fuels. So it is believed that these results tend to confirm that the test rig did successfully separate these fuels on the basis of loss of heat transfer performance as a result of heat exchanger fouling.

It was noted that the data of Figure 3 showed highest h_c values for fuel K26, which was the highest ranking of the group in CFR Fuel Coker rating as well, at 400 F-plus temperature conditions. Additionally, fuel K500 which produced the lowest h_c values fails the CFR Fuel Coker test at 400 F-plus temperature conditions - thus the separation in order of quality for the two extremes in the group was the same for both types of test. Thus an attempt at a numerical correlation seemed indicated for the complete group of JP-6 fuels, since fairly current CFR Fuel Coker ratings were available for these fuels. Figures 4 and 5 show the relationship between heat transfer coefficients obtained after one hour test time at 410-420 F fuel-out temperature in the small-scale recirculating flow thermal stability tester versus CFR Fuel Coker filter merit ratings and accumulated pre-heater deposit ratings at 400 F fuel-out temperature respectively. Considering the differences in approach towards measuring thermal stability represented by these data, the agreement was better than expected.

3. Evaluation of Fractions of a Borderline JP-6 Fuel

As a supplement to the studies of storage stability being carried on under this contract in which attempts are being made to identify the constituents of jet fuels causing losses in thermal stability with storage, a West Texas kerosine-alkylate JP-6 blend of borderline thermal stability (in terms of JP-6 requirements) was cut into three fractions boiling in the ranges: (1) IBP-360 F, (2) 360-400 F and (3) 400 F plus. These fractions were tested in the miniature recirculating flow jet fuel thermal stability test rig at a fuel outlet temperature of 300 F. The spent fuel samples were retained and subjected to chromatographic analyses in an attempt to establish what changes, if any, had occurred in these fractions as a result of the two-hour recirculating heating cycle. The results and interpretation of these analyses are discussed in detail elsewhere in this report, but the point to be made here is that this effort utilizing the small scale apparatus provided data for explanation of fuel degradation mechanisms using samples which could not have been made available in sufficient volume for evaluation in the CFR Fuel Coker. It has also demonstrated the applicability of this test technique to fuels varying considerably in volatility characteristics.

Data on the thermal stability performance of the three fractions described above are shown in Table I and graphically in Figure 6. The test rig effected a wide separation of these fuels in terms of heat exchanger fouling quality, the
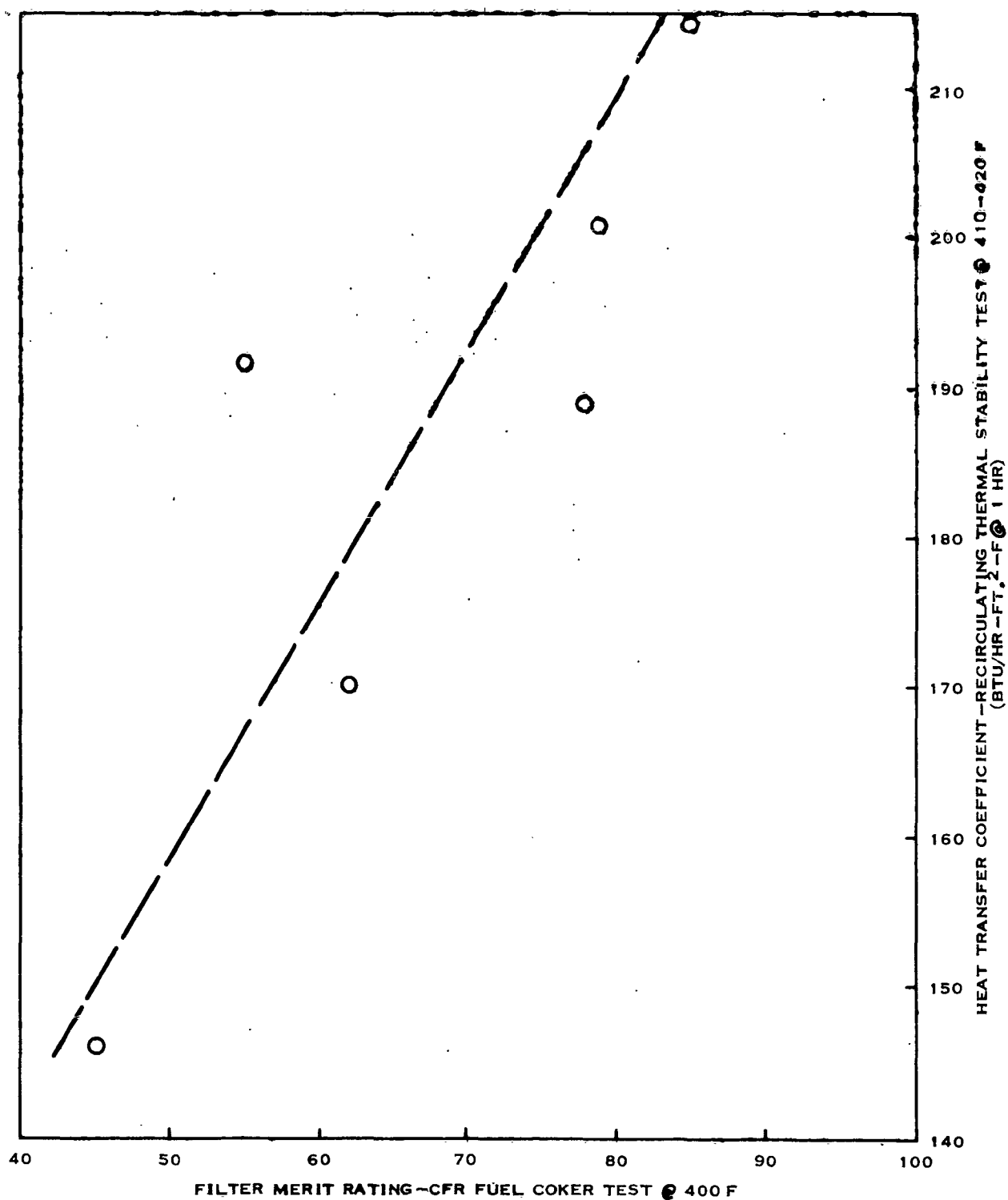
FIGURE 4

RELATIONSHIP BETWEEN THERMAL STABILITY RATINGS IN TWO TYPES
OF APPARATUS USING JP−6 TEST FUELS

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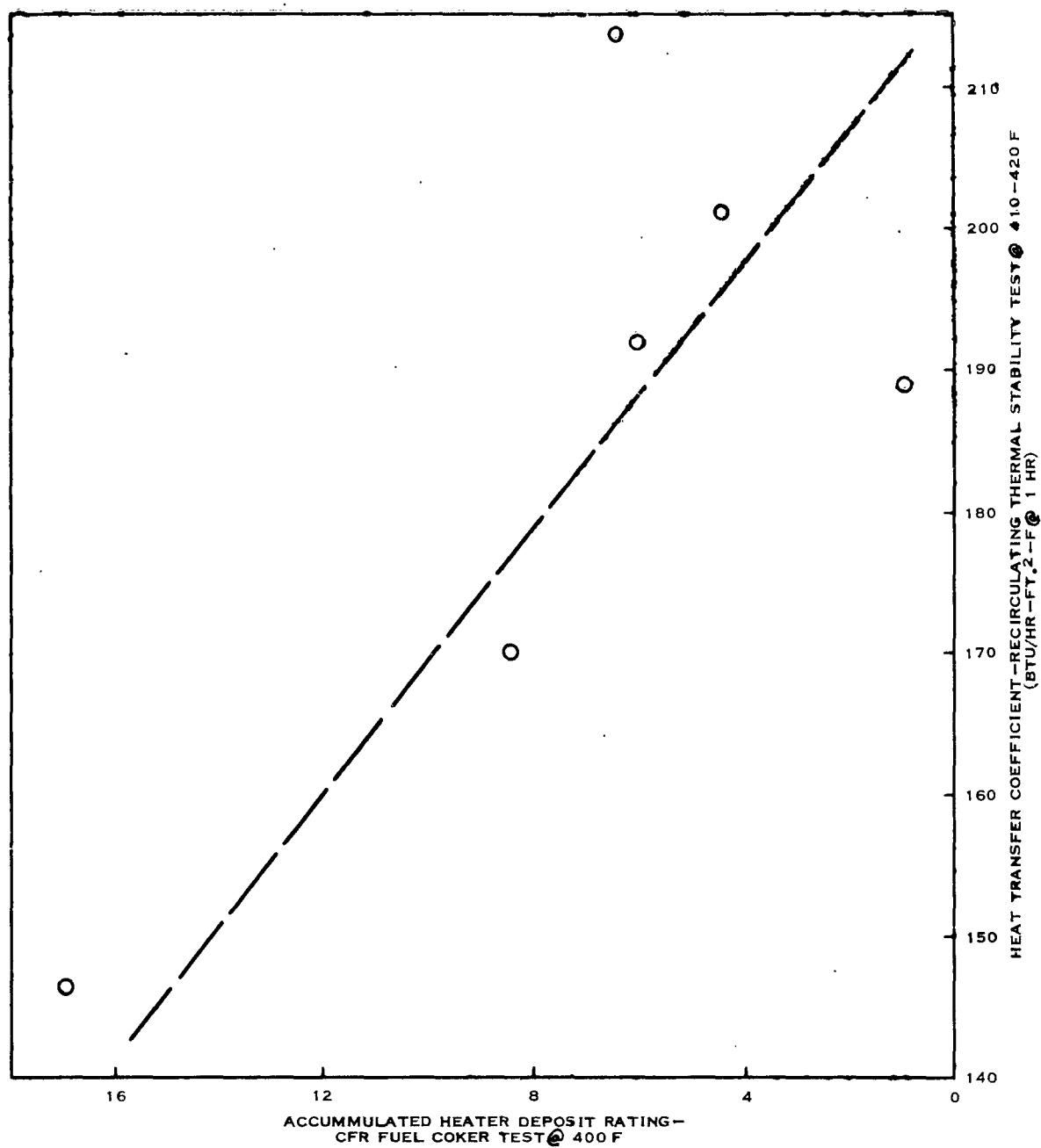
FIGURE 5
RELATIONSHIP BETWEEN THERMAL STABILITY RATINGS IN TWO TYPES
OF APPARATUS USING JP-6 TEST FUELS

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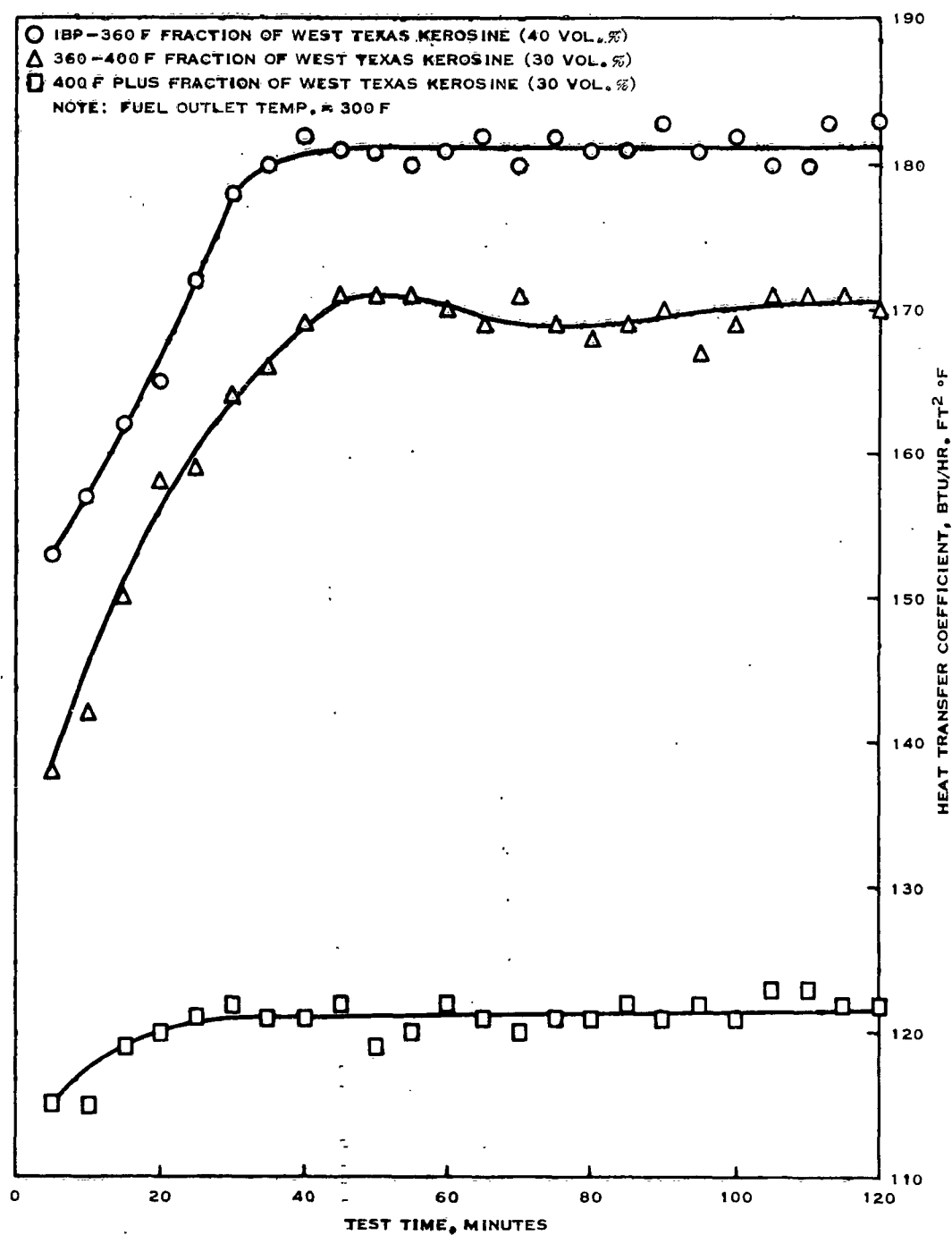
FIGURE 6
HEAT TRANSFER PERFORMANCE OF THREE FRACTIONS OF A WEST TEXAS
KEROSINE IN THE SMALL SCALE RECIRCULATING FLOW
JET FUEL THERMAL STABILITY TESTER

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lowest boiling fraction rating highest in stability, the middle boiling fraction somewhat less stable and the highest boiling fraction very much less stable. Thus, these results indicated the most unstable fuel constituents to be identified with the 400 F plus fraction, providing a very useful guide for the subsequent chemical analysis work.

4. Supplementary Design Considerations

The experimental data presented in the foregoing were largely obtained using an air-cooled after cooler, simply a length of coiled stainless steel fin tube. It became apparent that this job could be done more effectively (and more compactly) with a water cooled tube-and-shell heat exchanger in which the fuel passage was a single, straight-through, easily-cleaned passage, which is the installation pictured in Figure 1.

Another point investigated was the possibility of reducing the rather high heat flux level (571 Btu/in^2) employed in the tests at 410-20 F fuel-out temperature by adjusting heat exchanger dimensions, without of course reducing the rate of deposit accumulation too greatly. It appeared that a somewhat larger heat exchanger utilizing a heated tube of 3/16 inch diameter x 18 inch heated length operating in a 1/4 inch i.d. shell (as compared to the original 1/8 inch dia. x 7 inch length tube) would offer a suitable compromise of severity and operational ease. This design has been operated successfully at tube temperatures as high as 900 F with no undue operational problems. However, it was necessary, with increased heater tube length, to develop an insulator-sealing system which would allow slippage through the seals as the tube expanded upon heating. After trying a number of methods and materials it has been concluded that a satisfactory system consists of an ordinary metal tubing ferrule and nut seal at the hot (downstream) end of the exchanger and a pair of Viton O-rings at the cold (inlet) end. This system was found to provide excellent sealing and electrical insulation along with the desired tube slippage at elevated temperatures.

Some reduction in severity with this modified heat exchanger was achieved, accompanied by a significant reduction in the amount of deposition on the tube as compared to the deposition observed on the original 1/8 inch x 7 inch tube for the same fuel heating level and operating time. Although the desired decrease in severity was achieved by this design, it would, of course, be necessary to stretch out the running time in order to arrive at an equivalent degree of fouling and consequent loss of heat transfer performance at any given fuel-out temperature.

It also appears that the system pressure (240 psig) employed for the data obtained in the 1/8 inch x 7 inch heat exchanger may not have been high enough to prevent some degree of nucleate boiling at the heating tube surface with the JP-6 test fuels. The marked influence of changes in system pressure from 50 psig to 350 psig on heater tube inside wall temperature is shown in Table II. The effect was quite dramatic with tube temperatures decreasing with decreasing system pressure, indicating the presence of nucleate boiling at the wall of the heater tube. It should be noted that this effect was observed even in the face of increasing heat inputs occurring apparently as the result of tube cooling (and consequent decreasing electrical resistance) by evaporation of the fuel at its surface. It is probable that nucleate boiling occurred during at least

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TABLE II

EFFECT OF SYSTEM PRESSURE ON HEATER TUBE SURFACE TEMPERATURES IN THE

MINIATURE DYNAMIC THERMAL STABILITY TESTER

Heat Exchanger Dimensions: 1/8" o.d. x 7" Tube in 1/4" i.d. Shell
Fuel: BJ60-10-K27: Voltage Drop Across Tube: Constant 3.7 volts;
Flow: 1 gph

Pressure psig	Fuel In, °F	Fuel Out, °F	Tube (midway) °F	Heat Input Btu/hr.
350	84	385	762	1288
300	85	388	739	1295
250	85	392	705	1313
200	86	393	677	1326
150	85	398	632	1339
100	85	398	575	1358
50	85	391	472	1389

part of the test runs previously discussed and would explain some of the rather high values of heat transfer coefficient obtained during those tests. Thus the independent control of system pressure allowed by nitrogen gas pressurization of a closed recirculating fuel loop permits the investigation of fuel high temperature depositing characteristics under both non-boiling and boiling conditions.

The development of a test procedure based on deposit-insulating effects in a recirculating, flowing system was terminated at this point, having satisfactorily demonstrated the feasibility of this type of approach using one-liter fuel samples and apparatus quite simple in design by comparison with existing thermal stability test procedures. It is suggested that such an approach could be followed up with profit as a part of other Air Force sponsored test methods research in the jet fuel area.

B. Static Fuel Systems

The remainder of the time on test methods development under this contract is to be spent on static types of procedures emphasizing simplicity and small fuel sample requirements as primary criteria; the type of test which could be readily employed by research chemists involved in the fuel synthesis phases of the overall Air Force fuels research program, for preliminary screening of various high temperature fuel candidates. In addition, the application of a test of this nature to specification control purposes would offer obvious advantages over the present relatively cumbersome CFR Fuel Coker procedure, if satisfactory correlations could be demonstrated with test results in larger scale, more realistic, apparatus.

1. Background

There are many possible approaches to measuring effects of heating on the formation of insoluble resins or "gum" in hydrocarbon mixtures. When the problem of jet fuel temperature instability was first recognized, attention was given to the ability of conventional gravimetric existent and accelerated gum procedures to predict the performance of fuels in this respect. These techniques were found insufficiently sensitive to pick up the very small amounts of potential gum formers producing high temperature filter plugging in early versions of the CFR Fuel Coker apparatus and various like devices. It was noted that, while fuels rating marginal in gum content often rated poorly in CFR Fuel Coker filter plugging, the converse was not necessarily true -- many fuels rating very low in gum content also rated poorly in CFR Fuel Coker filter plugging performance (8). Whereas the present existent and potential gum test procedures produce an answer in terms of mg of gum present in 100 ml of test fuel sample, severe plugging of the CFR Fuel Coker filter can be caused by just a few mg of gummy material produced from 5 gallons of test fuel. Thus the failure of the gum test procedures to guard against this type of problem is no doubt in part due to inadequate sensitivity. However, other reasons may include the fact that physical characteristics of the deposits, not recognized by an evaluation based merely on gross weight per unit volume of fuel, such as particle size and adherent qualities, are important in determining their relative harmfulness in aircraft fuel systems.

Southwest Research Institute has done considerable work under both Navy and Air Force sponsorship on bomb-type static heating tests for jet fuel stability (9)(10)(11). The references cited show a progression from (1) a small scale

externally heated bomb in which insolubles were evaluated by filtration and weighing to (2) a larger volume bomb (one liter) so as to provide larger amounts of filtered residue for more accurate weighing and finally to (3) an internally heated bomb of intermediate volume (200 ml) in which the effects of the filtered residue were evaluated indirectly in terms of filtration time increase rather than gravimetrically. The latter device became the CRC bomb test, evaluated to a limited extent by the CRC-Fuels Thermal Stability Group Small Scale Apparatus Panel and by this laboratory working under Navy sponsorship (7). This test does avoid the limitations of bath-type heating where temperature conditions from 400-800 F are desired and also attempts a measure proportional to adherent qualities instead of merely gross weight of insolubles formed by heating. In addition, deposit laydown on the heater tube itself can be rated visually as in the CFR Fuel Coker test, though tending to be much lighter for a given fuel and temperature condition with the bomb heating times usually employed.

It has been found (7) that this test is capable of separating fuels in thermal stability quality if tests are made over a series of temperature conditions to establish a "threshold" failure level, though it is difficult to interpret a test result at any one temperature with this apparatus. Though this has some advantage in providing a rating in terms of a definite limiting fuel temperature, it does make the test somewhat more time-consuming than is desirable -- while the lightness of the heater deposits presents some difficulty in meaningful evaluation.

Preliminary experiments under the present contract (1) attempted measurement of the effects of deposits formed in the CRC Bomb (See Figure 7) on heat transfer to fuels of known CFR Fuel Coker performance characteristics -- using a modified heating tube containing internal thermocouples for indicating surface temperature. These were unsuccessful and the CRC Bomb assembly was abandoned as unsuitable for this type of measurement. However, attracted by the meaningfulness of a fuel thermal instability test based on deterioration in heat transfer through deposit-fouled surfaces, further efforts were made to evolve a static test procedure based on this type of effect (as was done with the dynamic recirculating flow procedure discussed earlier). This work is to be described in a separate section of this report and represents one of the two types of approach to a static thermal stability evaluation procedure selected to follow up under this contract.

Another, more indirect, type of effect which might be taken advantage of in a small scale test of the nature desired is the change in fuel optical characteristics before and after heating. Color changes are well recognized as sensitive indicators of chemical or physical changes involving only minor amounts of reactants. As applied to petroleum fuels, darkness in color has long been used as a rough guide to the probable instability characteristics of undyed products, particularly heating oils. However the quantitative significance of standard color tests for petroleum products, such as the Saybolt chromometer technique and the ASTM colorimeter method for darker products, are difficult to assess with respect to deposit problems in fuel handling equipment. Investigators at Cities Service R & D have developed a technique (12) for indirectly measuring the insoluble gum level of fuel oils by changes in optical density measurements (using 0.5 micron wavelength monochromatic light) before and after filtration

18

HEATER TUBE

SEAL

TO PRESSURE GAUGE, RUPTURE DISC AND VALVE

LIQUID LEVEL (COLD)

UPPER FUEL THERMOCOUPLE

POSITIONS FOR SUPPLEMENTARY MEASUREMENTS OF SURFACE TEMPERATURE WITH MODIFIED HEATER TUBE

HEATER SHEATH

LOWER FUEL THERMOCOUPLE
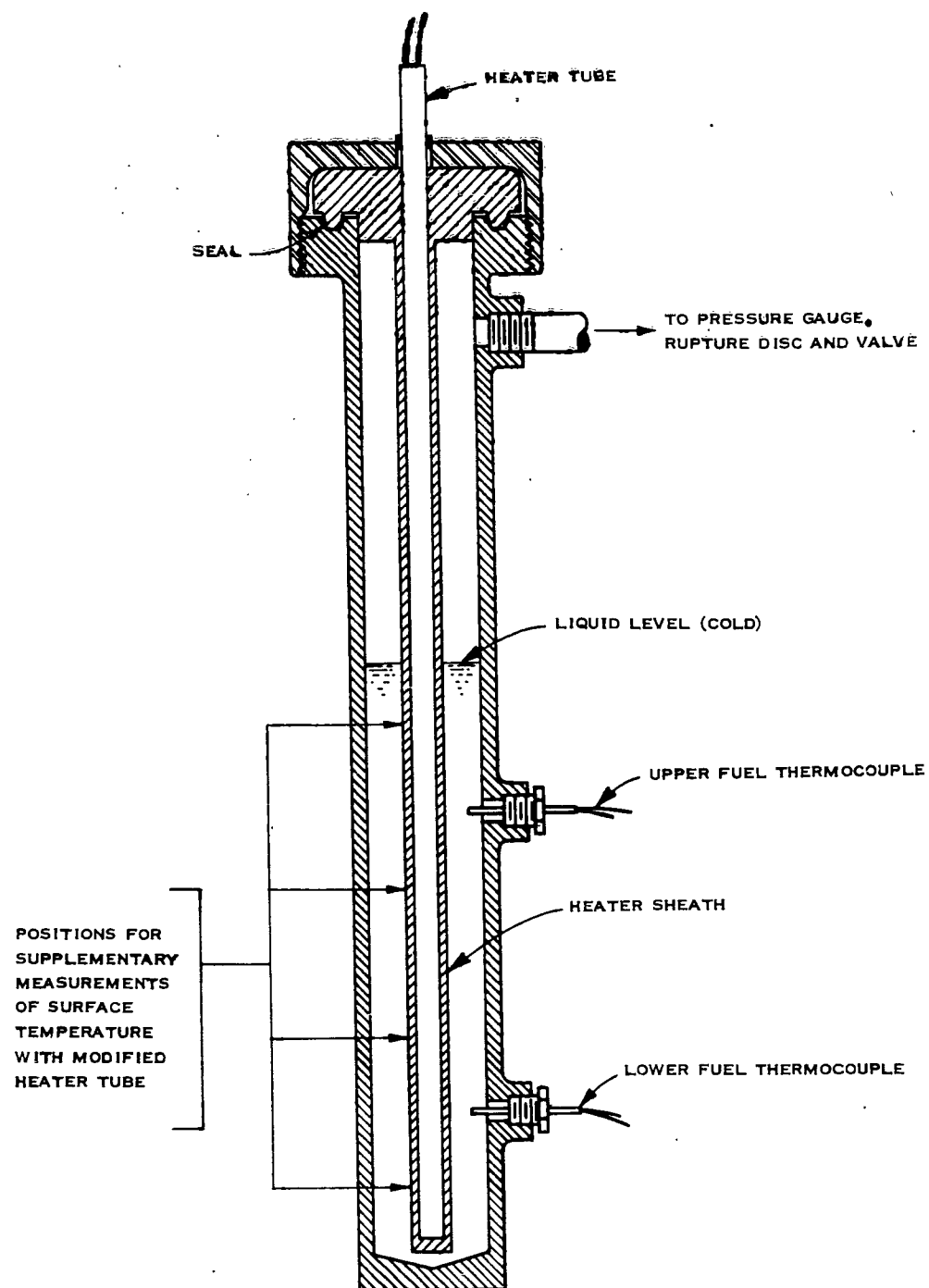
FIGURE 7
MODIFIED CRC THERMAL STABILITY BOMB ASSEMBLY

through a sintered glass 5-micron filter. By this means only a 20 ml sample need be filtered, versus at least 350 ml if insolubles are to be determined with comparable precision by direct weighing.

During work by this laboratory with the CRC Thermal Stability Bomb test it has been noted that the changes in fuel light transmission characteristics following heating (measured with a Fisher Electrophotometer using blue light) produced numbers separating several test fuels in approximately the same order of quality as the other more direct types of measurement did. Investigators at the University of Cincinnati[13] have employed the increase in ultraviolet light absorbency at 0.350 micron wavelength as an index of fuel thermal instability following heating, in a program attempting to pin down causes for thermal instability in JP-3 and JP-4 type jet fuels.

Research on the oxidation and formation of insolubles in diesel fuels has been carried out by Caterpillar Tractor Company[14] using a very similar technique. Here complete optical density versus wavelength curves were plotted over the range from 0.35 to 0.65 microns wavelength (using a Coleman spectrophotometer) for fuels after heating to temperatures up to 365 F. Marked increases in fuel optical density, particularly noticeable at 0.34-0.40 microns wavelength, followed heating in the presence of oxygen.

A somewhat different but related technique has been applied by Naval Research Laboratory to the study of stability problems with both diesel fuels[15] and jet fuels[16]. Here, the light scattering characteristics of fuels at various stages of thermally-induced degradation are employed as an index to the quantity of particulate matter present, using a 0.436 or 0.546 micron wavelength light beam and measuring the intensity of light scattered at a 45° (forward) angle from the incident beam. As applied to jet fuels the procedure employed by NRL consists of prefiltering the fuel through a 0.45 micron Millipore filter paper to remove any particulate material initially present, heating in a CRC Thermal Stability Bomb, followed by measurement of scattered light intensity. The earlier NRL studies on diesel fuels were followed up by this laboratory working under Navy contract with regard to the application of the light scattering technique to jet fuel stability problems[17]. It was concluded that the excellent sensitivity of this type of measurement to the appearance of small solid particles in fuels warranted further efforts to apply it to jet fuel stability problems.

A type of measurement sensitive to particles representing potential deposit-formers at an even earlier stage of growth is represented by electron microscopy. Southwest Research Institute has investigated[11][18] this means of indicating incipient thermal instability and have shown a degree of correlation between temperature limits based on differences in particle appearance in fuels heated through a range of temperature conditions in very-small-volume (3 ml approx.) "bombs" and ratings in the High Temperature Research Fuel Coker. Electron microscopy has also been applied to the measurement of stability quality in diesel fuels for railroad usage[19], where the ability to actually "see" small particulate

solids allows evaluation of the effects of detergent-dispersant additives on low grade fuels containing relatively gross amounts of gum or sludge-forming constituents.

Thus the application of optical techniques to measurement of instability in petroleum fuels has received considerable attention in the past -- and it was decided that this type of measurement, offering as it does excellent sensitivity to effects produced by very small amounts of reacting material, represented a second approach to pursue under the present assignment. Since methods such as these merely reflect something which exists in the complete fuel, it must be recognized that meaningfulness with regard to actual engine deposition problems must be established empirically. Experimental work carried out to date by this laboratory on the application of optical measurements to a small volume jet fuel thermal stability test will be discussed separately.

2. Deposit Insulating Effects

Following the attempts mentioned earlier to employ the CRC Thermal Stability Bomb for measuring deposit insulating effects, it was decided to devise a static bomb of somewhat different design which would adapt itself somewhat better to this type of measurement. The first of these is shown in Figure 8 and is in principle comparable to the heated section employed in the recirculating flow tester previously discussed (Figure 1). A 1/8 inch stainless steel tube was employed both as deposit surface and heat source by direct resistance heating with low voltage-high amperage AC current. Rubber-asbestos gaskets provided both sealing and electrical insulation for the heated tube at each end. The heated portion of the apparatus was maintained liquid full and the offset section provided added reservoir capacity for expansion purposes. Temperature of the tube itself was indicated by two i.c. thermocouples inserted coaxially from either end, while the liquid temperature was indicated by thermocouples introduced through the sides of the bomb at corresponding axial locations. Using a 50 ml fuel sample volume, with 1/2 inch pipe as the outer shell, it was found that heating tube surface temperatures as high as 900 F failed to produce sufficient deposit laydown to cause any change in the fuel temperature-surface temperature relationship. It was concluded that the ratio of the heating tube surface area to the available mass of deposit from this small a fuel sample was too high to permit build up of deposits in depth such as to measurably influence heat transfer. Therefore a larger version of this apparatus was assembled allowing an 800 ml fuel charge, retaining all the mechanical features indicated in Figure 8, using 2-inch pipe as the outer shell. Using this unit it was possible to lay down deposits rating No. 4 or worse completely covering the surface of the 1/8 inch heater tube following a three-hour heating cycle with a low thermal stability quality kerosine. This still produced no significant effects measurable in terms of temperature, and,in addition,800 ml is considered an un-desirably large amount of fuel to heat batchwise in a small sample test procedure.
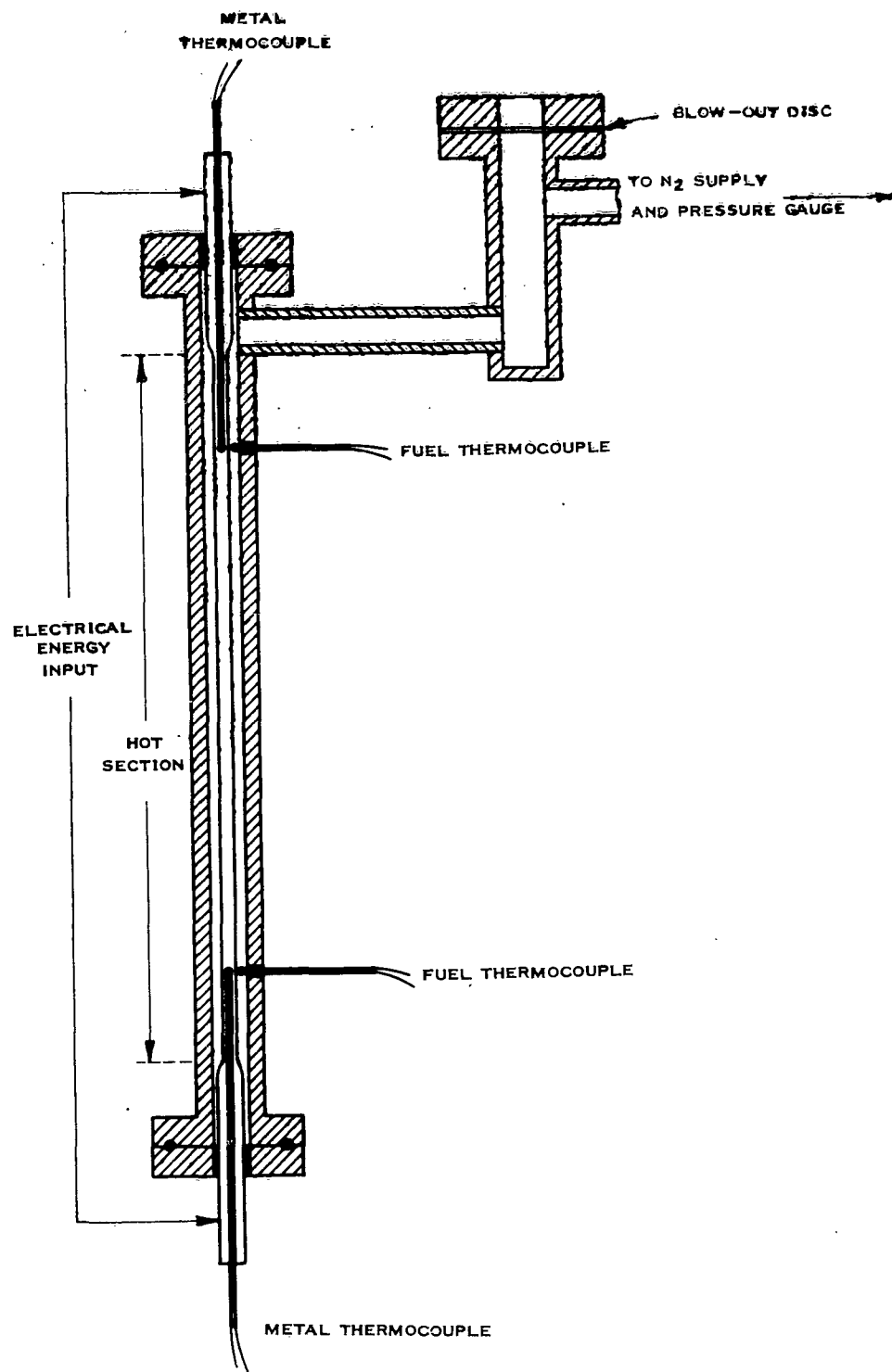
FIGURE 8
50 ML INTERNALLY HEATED JET FUEL THERMAL STABILITY BOMB

Therefore, the next attempt towards a static test based on deposit insulating effects moved in the other direction, that is a reduction in the area of the heating surface to (1) permit given small masses of deposit to build up in greater depth and (2) minimize conduction paths for external heat losses masking deposit effects. Keeping in mind the desire for simplicity of apparatus it was decided that a technique utilizing a short section of small diameter heated wire immersed in fuel would offer a large increase in responsiveness (or sensitivity) while remaining quite simple. By selecting material with a suitable temperature coefficient of resistance this wire could be used not only as the heating element but also as a resistance thermometer for measurement of wire surface temperature. Measurement of voltage drop across the wire and current flow through the wire would establish both heat input and resistance. Changes in wire resistance could be converted to changes in wire temperature. It was expected that deposit laydown would cause an increase in wire temperature and possibly a decrease in fuel temperature, as a result of the insulating effect of the deposits, assuming operation at constant heat input.

Figure 9 shows a "breadboard" apparatus assembled to evaluate this approach, using an open fuel reservoir (400 ml glass beaker). The "hot section" consists of a 2 1/8 inch length of 0.005 inch diameter nickel wire having a resistance of 0.4 ohms at 70 F. This wire is supplied with current from a 115 V - 12 V step-down transformer. Voltage drop is measured across the wire and an ammeter is placed in series in the secondary circuit of the transformer. Secondary voltage is adjusted by means of a Variac placed in the primary circuit of the transformer. Fuel temperature is measured by an iron-constantan thermocouple placed at the center and 1/4 inch above the heated wire. Ideally the operation of this apparatus would consist of setting a constant heat input (wattage) and observing changes in wire and fuel temperatures with time. Since a suitable wattmeter was not available at the time this work was begun and since it is difficult to predict the necessary combination of voltage and amperage to maintain a fixed wattage by manual adjustment of the variac, it was decided to operate at a constant voltage drop across the wire and simply accept the loss in wattage as the resistance of the wire increased with increasing temperature. It was thought that the effects of deposit-fouling would be detected even in the face of slightly decreased heat input with a system as responsive as this -- which was subsequently confirmed.

Since these preliminary tests used an open fuel reservoir, it was necessary to employ a fuel of sufficiently low volatility to prevent excessive boiling at the wire, loss of vapors etc. The fuel selected was an Air Force HTF fuel previously supplied to Phillips for use under Contract AF 33(616)-5543, identified as HTF-16 and described as a paraffinic light lube oil. This fuel is basically high in thermal stability. In order to provide variations in thermal stability two blends were prepared using HTF-16 as base fuel with 1 per cent and 2 per cent (wt.) ASTM alpha methyl naphthalene added as a contaminant. The base fuel was expected to be degraded in thermal stability by addition of the AMN, since this has been found to be the case in CFR Fuel Coker tests with similar blends.

23
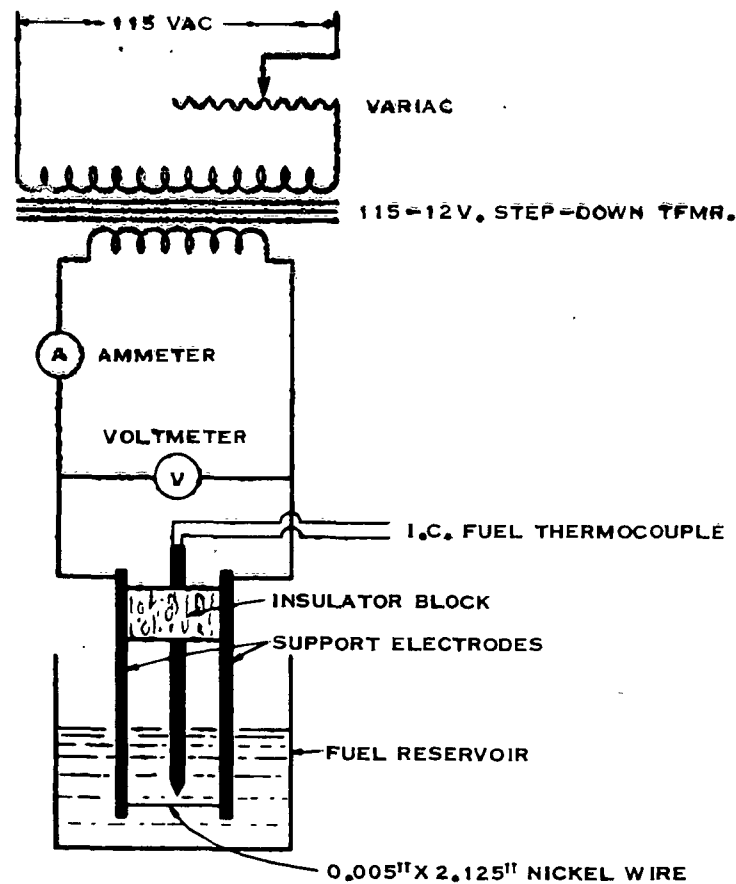
FIGURE 9
MODEL HOT-WIRE JET FUEL THERMAL STABILITY TESTER

24

Table III summarizes selected experimental data obtained with these fuel blends, and with an aged West Coast kerosine fuel as well. Figure 10 shows wire temperature and fuel temperature plotted as functions of time for the HTF-16 fuel with and without the AMN contaminant. It is shown that wire temperatures for both of the blends containing AMN began to rise sharply after about 100 minutes of operation while the base fuel itself leveled off in wire temperature at about this point. Thus it does appear that deposit insulating effects were sensed by this technique -- the rise in temperature occurring in the proper order of known thermal stability quality based on amount of alphamethylnaphthalene present. A rating could be based either on wire temperature level at some given time period beyond 120 minutes or on an "induction period" principle.

Fuel temperatures appeared slightly lower for the two poorer fuels at the end of the heating period, though this change was probably too slight to be applied towards a fuel rating.

As a follow-up to the tests described above a fourth test was conducted on a more realistic (and more volatile) fuel, a low thermal stability quality West Coast kerosine. The results of this test are shown in Figure 11. Again the sharp rise in wire temperature with the incidence of deposition was observed. Operationally this test was marginal, however, because of excessive boiling at the wire surface and attempts to run a similar test on a known stable fuel of comparable volatility were unsuccessful because of persistent wire burn out. Obviously, the use of such a technique for rating practical aviation turbine fuels would require that the fuel be put under sufficient pressure to retard excessive boiling at test temperatures. It is believed, however, that these tests have served to demonstrate the feasibility of such an approach to rating fuel thermal stability quality and it would appear, that further efforts in this area would be desirable. A revised version of this apparatus has been assembled incorporating an enclosed fuel reservoir to permit operation under pressures sufficient to prevent local boiling at the wire with JP-grade fuels.

3. Heat-Induced Optical Changes in Fuels

As previously pointed out, the application of optical techniques to measurement of instability in petroleum fuels has received considerable attention in the past (references 12, 13, 14, 15, 16 and 17) and it appeared that some attention should be given to such techniques in the present assignment. This seemed particularly desirable in view of the adaptability of such techniques to very small sample sizes although some sacrifice of realism would be required in the sense of not actually concentrating the insolubles or potential gum-forming materials. Of course, because of this it is obvious that the significance of such techniques with respect to engine performance would have to be established empirically.

25

TABLE III

HEAT TRANSFER DATA OBTAINED WITH THE STATIC HOT WIRE THERMAL STABILITY TESTER

Dimensions – 0.005" Dia. x 2 1/8" Nickel Wire, 0.4 ohm Resistance @ 70 F
Pressure – Atmospheric
Applied Voltage – 6
Fuel Charge – 250 Ml

Run	Fuel	Time, Min.	Amperage	Wattage	Ohms Wire Resistance	Wire Temp., F	Fuel Temp., F
5	Paraffinic Light Lube Oil (HTF-16)	0	5.10	30.60	1.176	649	51
		60	4.85	29.10	1.237	696	223
		150	4.70	28.20	1.277	725	233
6	HTF-16 Plus 1 Wt.% ASTM α-Methyl Naphthalene	0	5.10	30.60	1.176	649	60
		60	4.90	29.40	1.224	685	224
		150	4.40	26.40	1.364	792	224
4	HTF-16 Plus 2 Wt.% ASTM α-Methyl Naphthalene	0	5.10	30.60	1.176	649	67
		60	4.90	29.40	1.224	685	228
		150	4.10	24.60	1.463	865	222
			Applied Voltage – 5.4				
8	Aged West Coast Kerosine (G593D)	0	6.10	32.94	0.8852	432	53
		60	5.80	31.32	0.9310	466	223
		150	4.60	24.84	1.1739	648	217

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WIRE: .005" DIA. NICKEL—0.4 OHM @ 70 F
PRESSURE: ATMOSPHERIC
FUEL CHARGE: 250 ML
○ HTF—16 —PARAFFINIC LIGHT LUBE OIL
△ HTF—16 + 1% (WT.) ALPHA METHYL NAPHTHALENE
□ HTF—16 + 2% (WT.) ALPHA METHYL NAPHTHALENE

WIRE TEMPERATURES

FUEL TEMPERATURES

TEST TIME, MINUTES

TEMPERATURE, °F
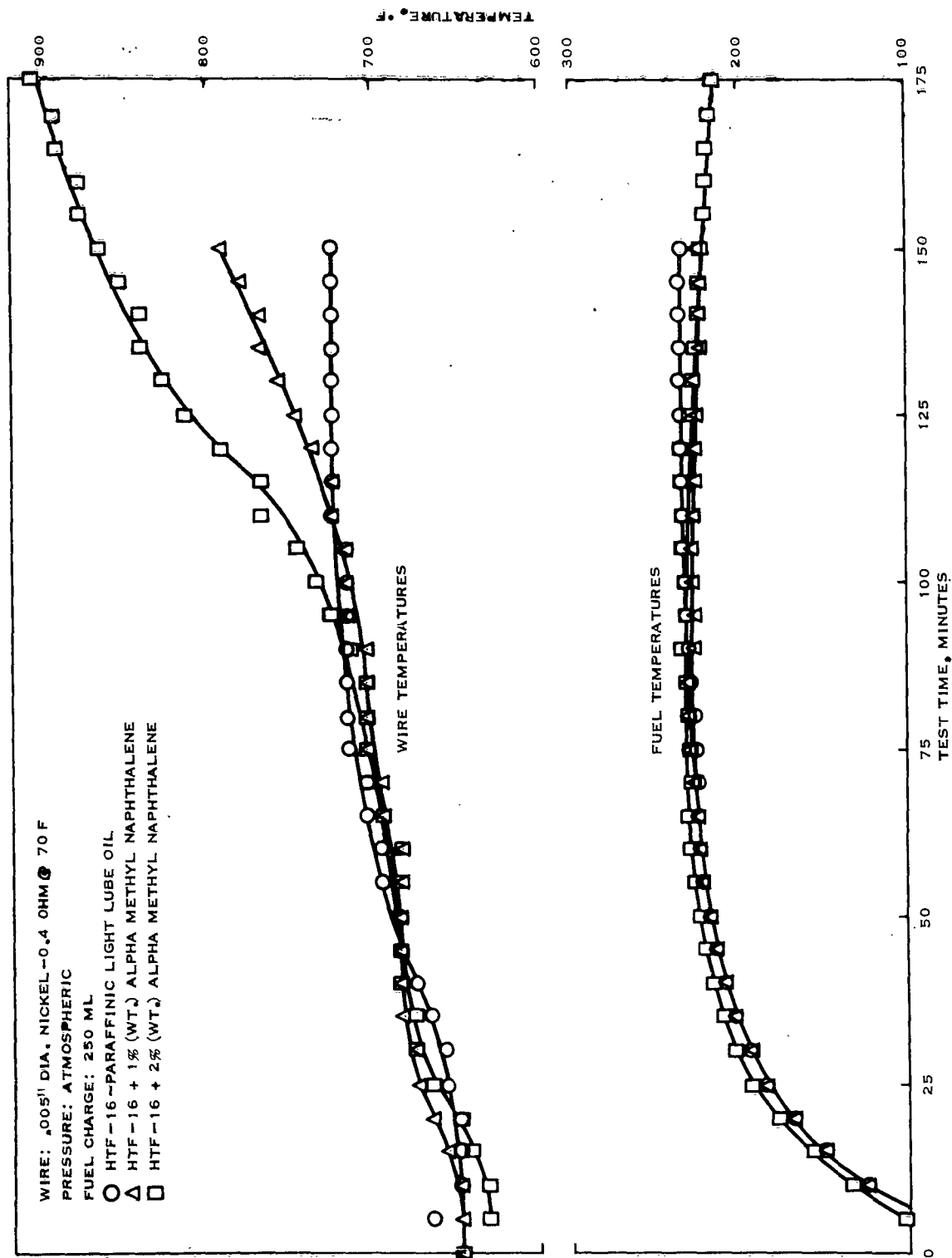
FIGURE 10
EVALUATION OF THERMAL STABILITY BY MEANS OF HEAT TRANSFER LOSS FROM HOT WIRE

27
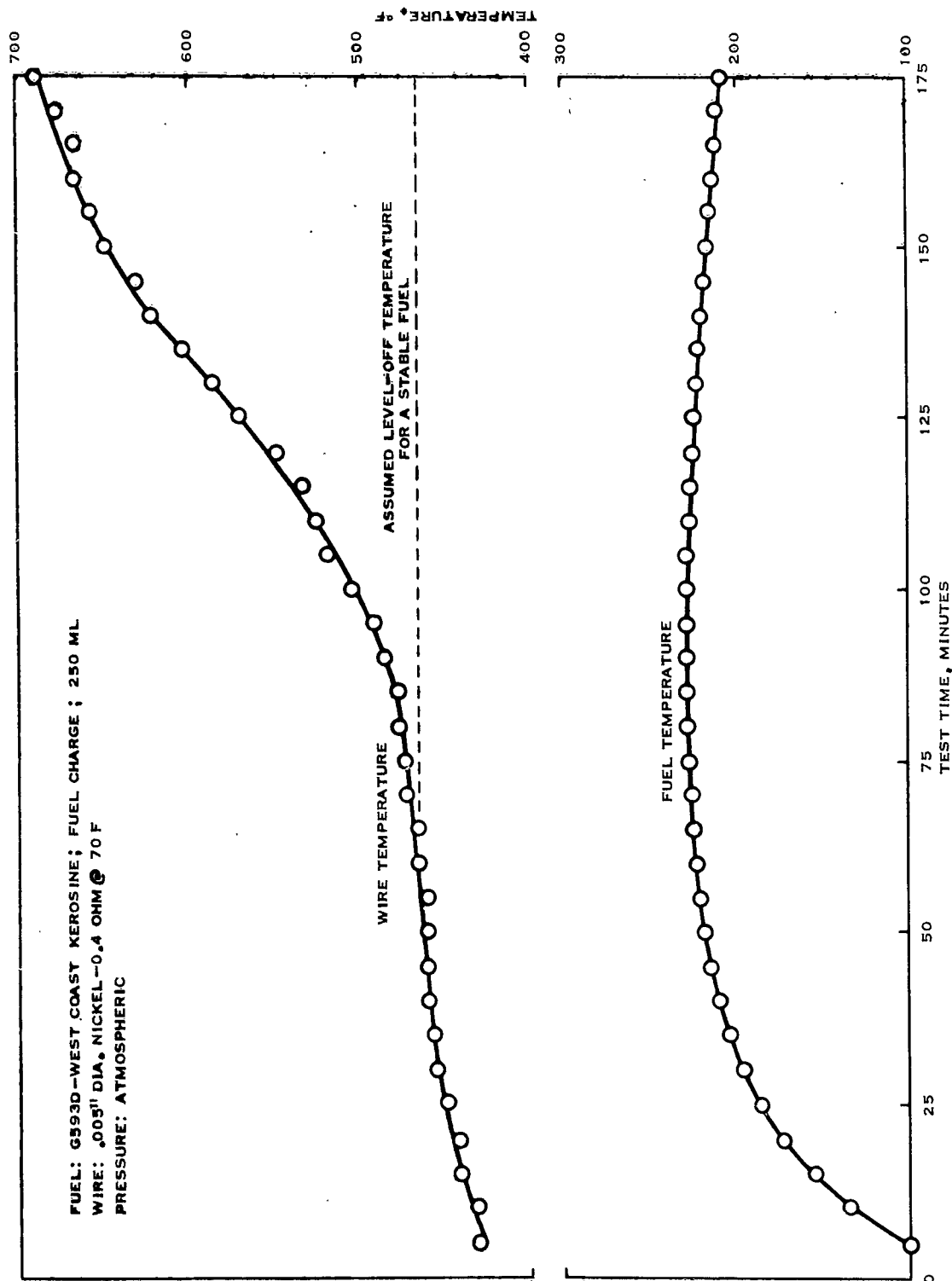
FIGURE 11

EVALUATION OF THE THERMAL STABILITY OF A WEST COAST KEROSINE BY THE HOT WIRE TECHNIQUE

28

During the past quarter under Contract AF 33(616)-7241 efforts were inaugurated to pursue the optical approach. For this purpose the miniature bomb shown in Figure 12 was designed and fabricated. This cylindrical bomb is constructed entirely of 304 stainless steel with threaded closures at each end suitably cut with tongues and grooves to allow the use of deformable aluminum washers for sealing. A coaxial tubing duct has been provided as a combined pressure tap and fuel thermocouple entry. Sizing is such as to allow the use of a 5 ml fuel sample with 10 ml outage in the main chamber. In use this bomb assembly is lowered into a preheated vertically mounted electrical tube furnace and the furance tube is then sealed at both ends with asbestos plugs. In this way the bomb is heated primarily by the radiation mode. Suitable instrumentation is provided for measurement of fuel and furnace temperatures and bomb pressure. By pre-calibrating the furnace temperature versus fuel temperature it has been found possible to repeatably predict the furnace temperature necessary to arrive at the desired fuel temperature in any given time. The heating procedure then simply amounts to preheating the furnace to the temperature indicated as necessary by the calibration curve and lowering the fuel charged bomb into the furnace leaving it there for a period of twenty minutes, after which time the fuel will have reached the desired temperature. The bomb is then raised out of the furnace, cooled in an air stream and the sample is removed for rating.

Preparation of the bomb prior to the heating cycle includes thorough brushing with hot water-detergent solution followed by rinsing in hot water. The bomb is then rinsed in acetone to remove the water, brushed, rinsed with acetone and air dried. The test fuel is prefiltered using 0.45 micron Millipore filter paper and aerated. Following aeration, exactly five milliliters of the fuel are placed in the bomb and the bomb is then sealed, pressurized to 50 psig with nitrogen and the assembly is placed in position ready for the heating cycle. Nitrogen pressurization has been found necessary to prevent excessive vaporization at higher temperatures. In the work carried on thus far the heating period has been arbitrarily held constant at 20 minutes. At the end of the 20 minute period the bomb assembly is removed from the furance cooled in an air stream and the sample is removed for rating. Rating is carried out first on the raw heated sample as poured from the bomb and then re-rated after filtering through 0.45 micron Millipore paper. Thus, some expression of the extent of formation of filterable material as a result of heating the fuel is available by comparison of the ratings before and after filtration.

Concerning the type of measurement to be made on the complete fuel after heating as an index of thermal instability, the objectives of the present assignment make it desirable to minimize the need for very specialized types of instrumentation. From this standpoint the use of electron microscopy or light scattering appeared less desirable for application to a semi-standardized test for use in more than one laboratory than the somewhat more indirect types of measurement represented by light transmission or optical density. Therefore, in the present program a Bausch and Lomb "Spectronic 20" spectrophotometer was employed to obtain measurements of the light transmittance of the heated samples from the 5 ml bomb at wavelengths varying from 340 to 650 millimicrons. This permitted the establishment of the optimum wavelength for best sensitivity to the heat-induced changes in the fuels by plotting transmittance versus wavelength curves. Based on the work of Professor Orchin at the University of Cincinnati (13) this was expected to occur near a wavelength of 350 millimicrons and results to be subsequently discussed will be seen to have confirmed this expectation.

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TO N_2 PRESSURE AND POTENTIOMETER

1/4" SS TUBING = 0.035" WALL

MILLED FLATS
FOR WRENCH

DEFORMED ALUMINUM WASHERS

1/2 "

2 1/2 "

3/4 "

1 "
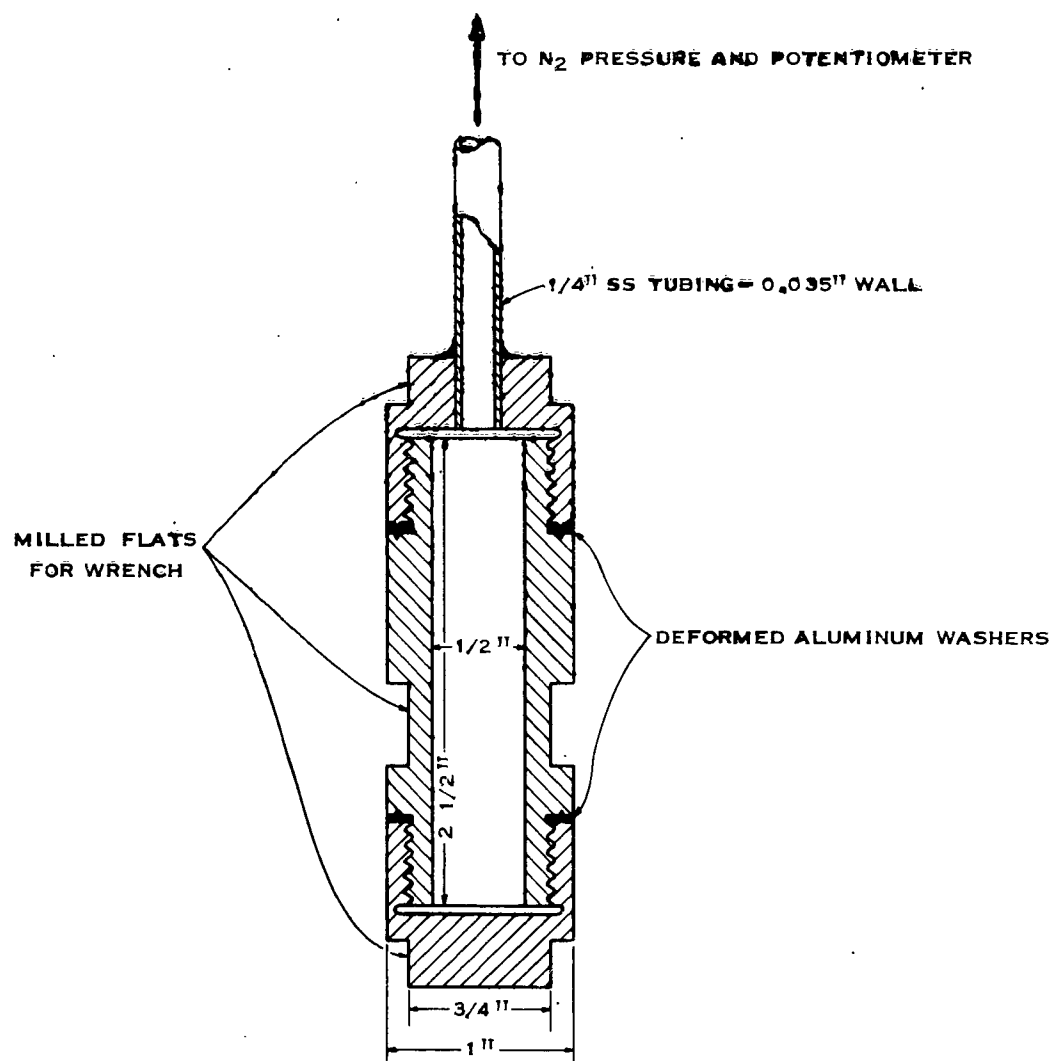
BOMB MATERIAL — 304 STAINLESS STEEL

NOTE : DURING TEST CYCLE AN IRON — CONSTANTAN THERMOCOUPLE
IS INSERTED INTO BOMB THROUGH 1/4" TUBE WITH
JUNCTION POSITIONED 3/8" ABOVE SURFACE OF BOTTOM
CAP.

FIGURE 12
FIVE MILLILITER EXTERNALLY HEATED JET FUEL THERMAL STABILITY BOMB

The test fuels selected for the preliminary investigations using the 5 ml bomb technique include five of the JP-6 fuels included in the storage program, K26A, K27A, K28A, K29A and K30A. Because of the timing of the start of this work it was necessary to use these six months sealed storage (110 F) samples, for which reasonably current CFR Fuel Coker ratings were available for comparison. Included also were a very stable isoparaffinic alkylate of JP-5 boiling range, BJ61-8-B1, and a minimum quality (from the thermal stability standpoint) JP-6 fuel supplied to Phillips by General Electric Company, BJ61-10-K1. This fuel is one which General Electric has found to be marginal with respect to its effect on heat exchanger performance in tests conducted in full-scale heat exchangers in their laboratories.

Discussion of Test Results

The data obtained thus far with the 5 cc bomb are shown in Figure 13 through 26 as plots of per cent light transmittance (using ASTM Grade isooctane as standard) versus wavelength for both the unfiltered and filtered samples after heating to temperatures ranging from 300 F to 550 F and in some cases as high as 650 F. The principal points brought out by these figures are (1) the generally consistent trend toward reduced transmittance with increasing fuel temperature, thus indicating the desired sensitivity to heating, and (2) the indication that optimum sensitivity seems to occur at approximately 350 millimicrons as suggested by the work of Orchin (13). Additionally, it is important to note that the expected decrease in transmittance would hold true only below 375 millimicrons in the case of K28A, definitely established by CFR Fuel Coker tests as the most unstable fuel in this group. Thus, it appears that the optimum wavelength in terms of both temperature sensitivity and known performance is 350 millimicrons and for this reason subsequent analyses of these data have been based on transmittance at this wavelength.

Considering next the factor of formation of filterable material in the heated fuels, the reader is referred to Figure 27 wherein the difference in transmittance before and after filtration has been plotted against fuel temperature. After only a cursory inspection of this plot it becomes apparent that the formation of filterable materials was largely random in these tests, as indicated by light transmittance, and regardless of whether this randomness is due to actual random formation of these materials or a manifestation of the vagaries of making the measurement in this way, it would appear that the filtration step in the test procedure would yield only negligibly useful results. However, it is interesting to note from Figure 27, that, in general, the maximum amount of filterable material seemed to be formed in most of the fuels at a temperature of about 400 F. At lower temperatures it would appear that less filterable material was formed and at temperatures above 400 F either less was formed or the temperature and nature of the material formed were such as to allow the material to redissolve. This peaking of filterable material is not unknown but has been observed previously during work conducted with the CRC Thermal Stability Bomb (7) (16). At any rate it would seem desirable in the interest of brevity, to eliminate the post-filtration step in future testing and to consider this test, and tests of similar nature, as simply capable only of heralding the formation of deposit precursors.

In order to better consider the relative performance of the several fuels tested by the 5 cc bomb optical technique it was considered desirable to plot their

31
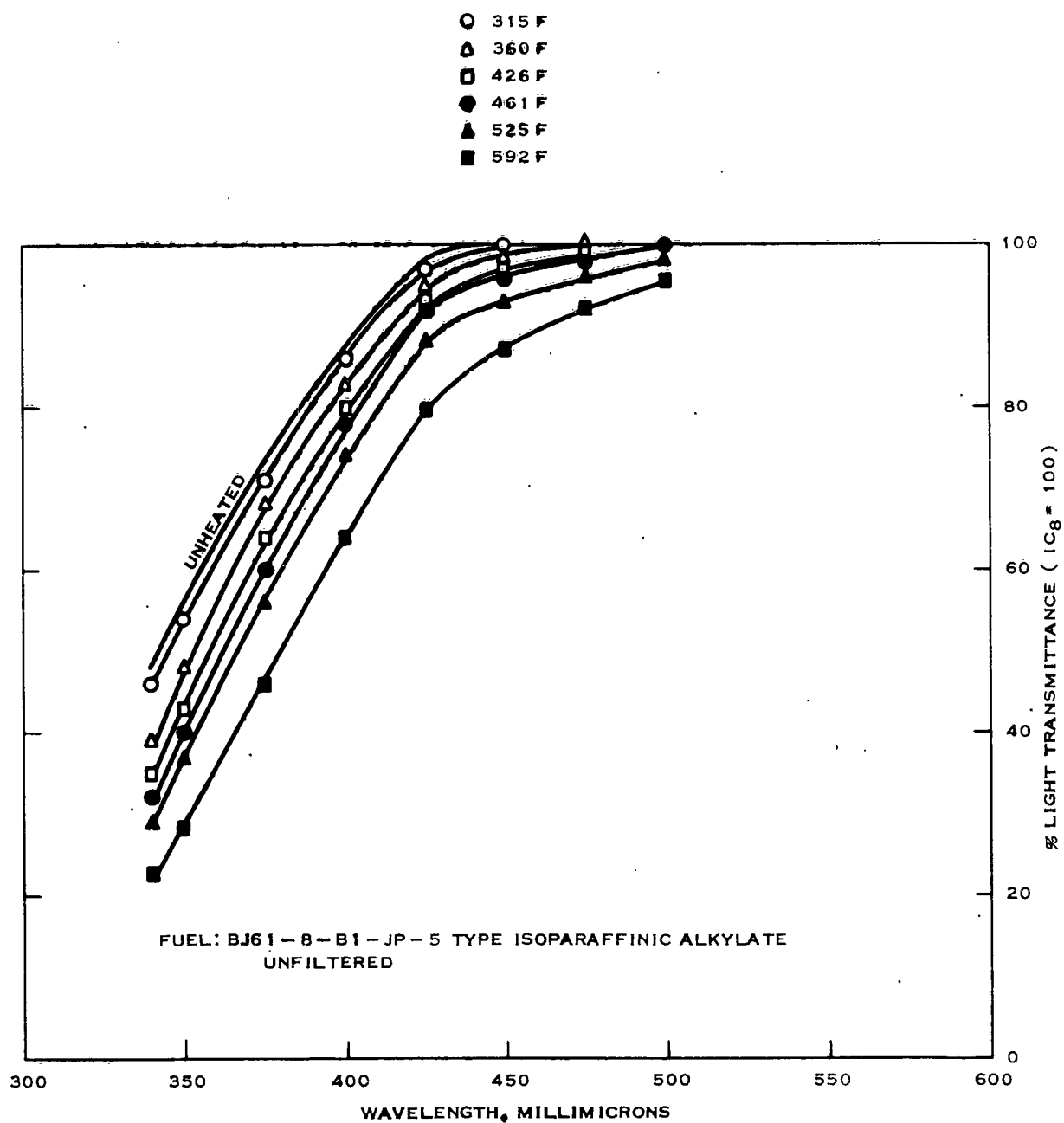
FIGURE 13
EFFECTS OF 20 MINUTE HEATING CYCLES IN THE 5 ML THERMAL
STABILITY BOMB ON LIGHT TRANSMITTANCE THROUGH JET FUELS
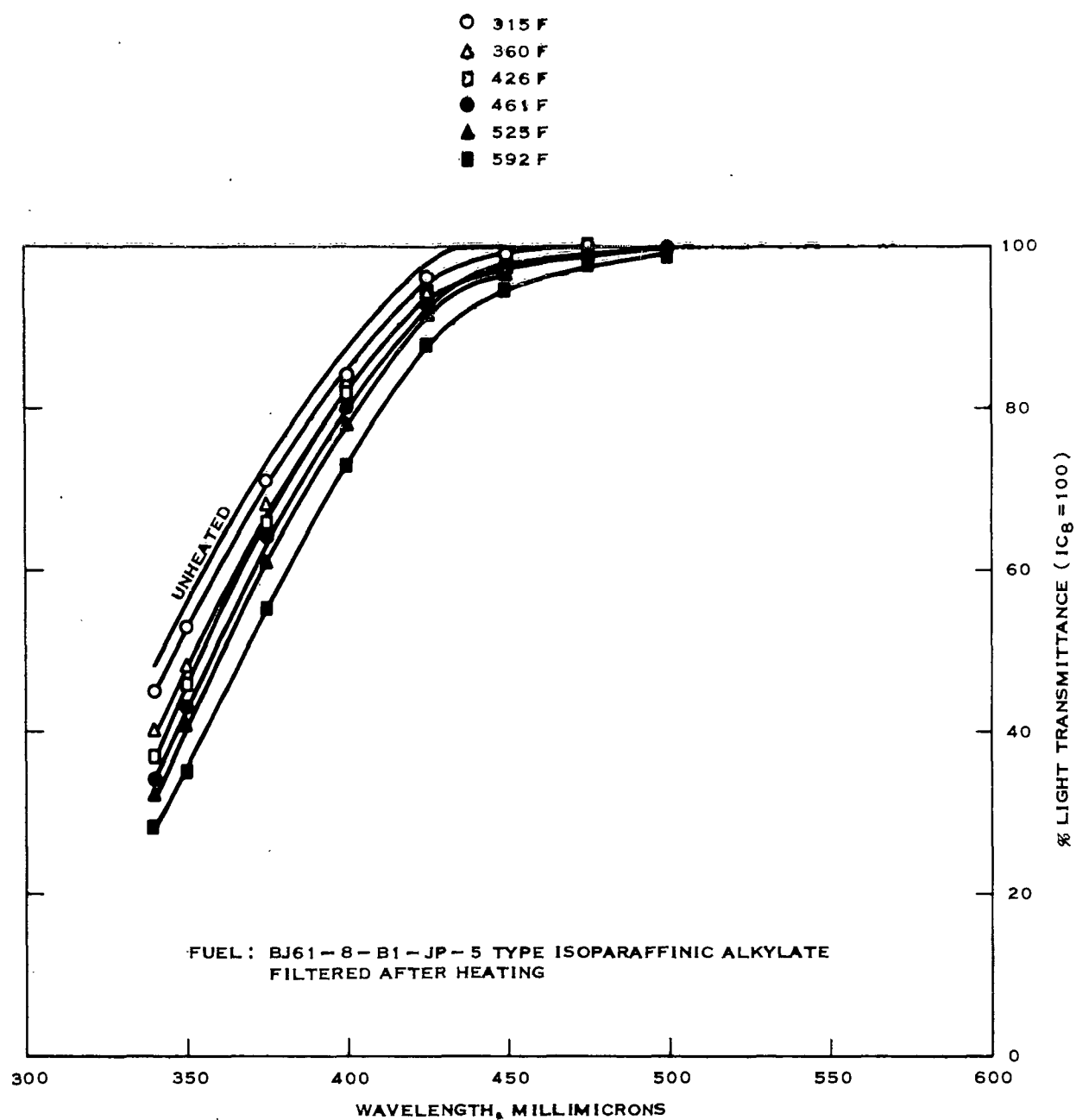
FIGURE 14

EFFECTS OF 20 MINUTE HEATING CYCLES IN THE 5 ML THERMAL
STABILITY BOMB ON LIGHT TRANSMITTANCE THROUGH JET FUELS
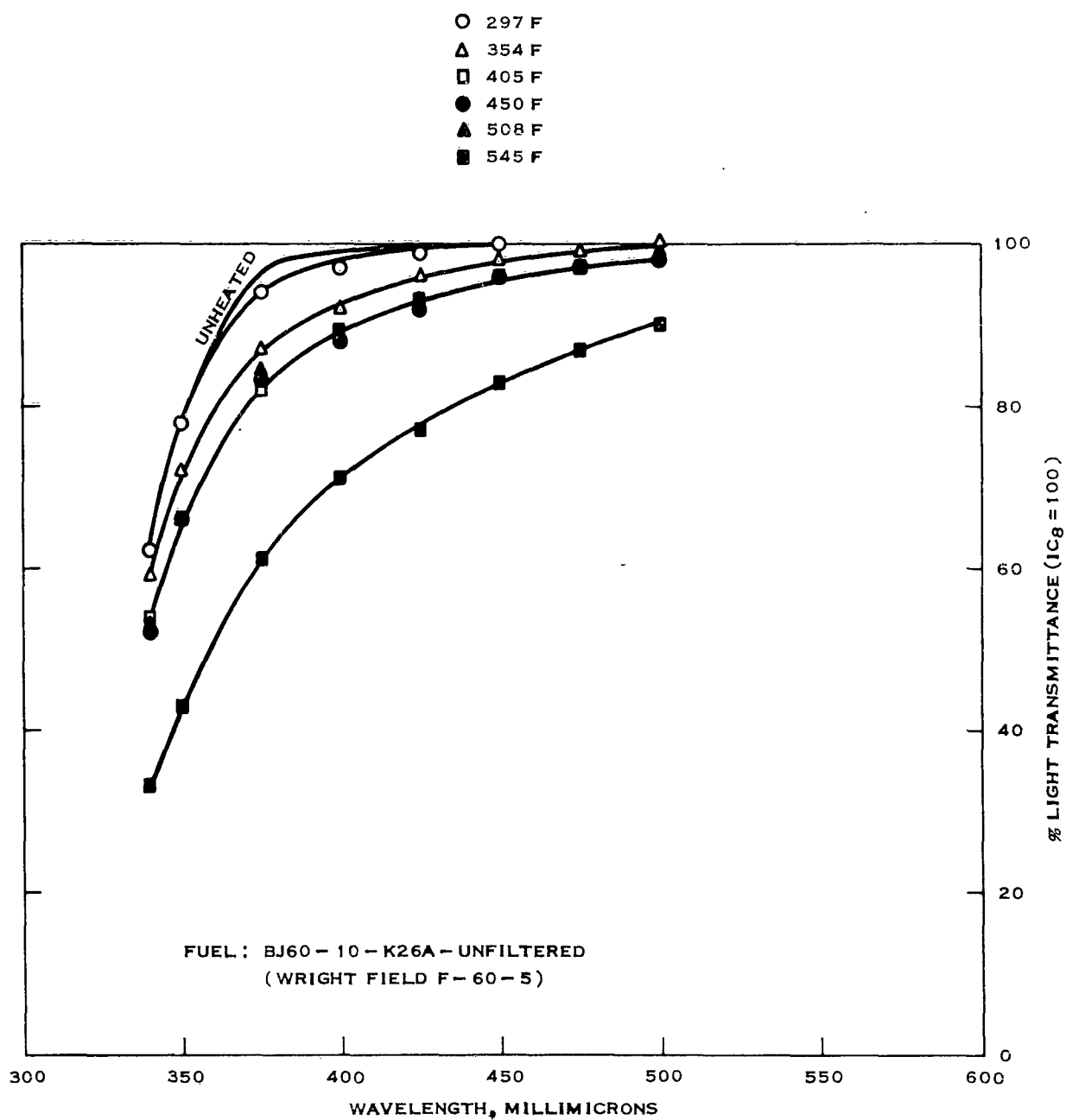
FIGURE 15
EFFECTS OF 20 MINUTE HEATING CYCLES IN THE 5 ML THERMAL
STABILITY BOMB ON LIGHT TRANSMITTANCE THROUGH JET FUELS

34
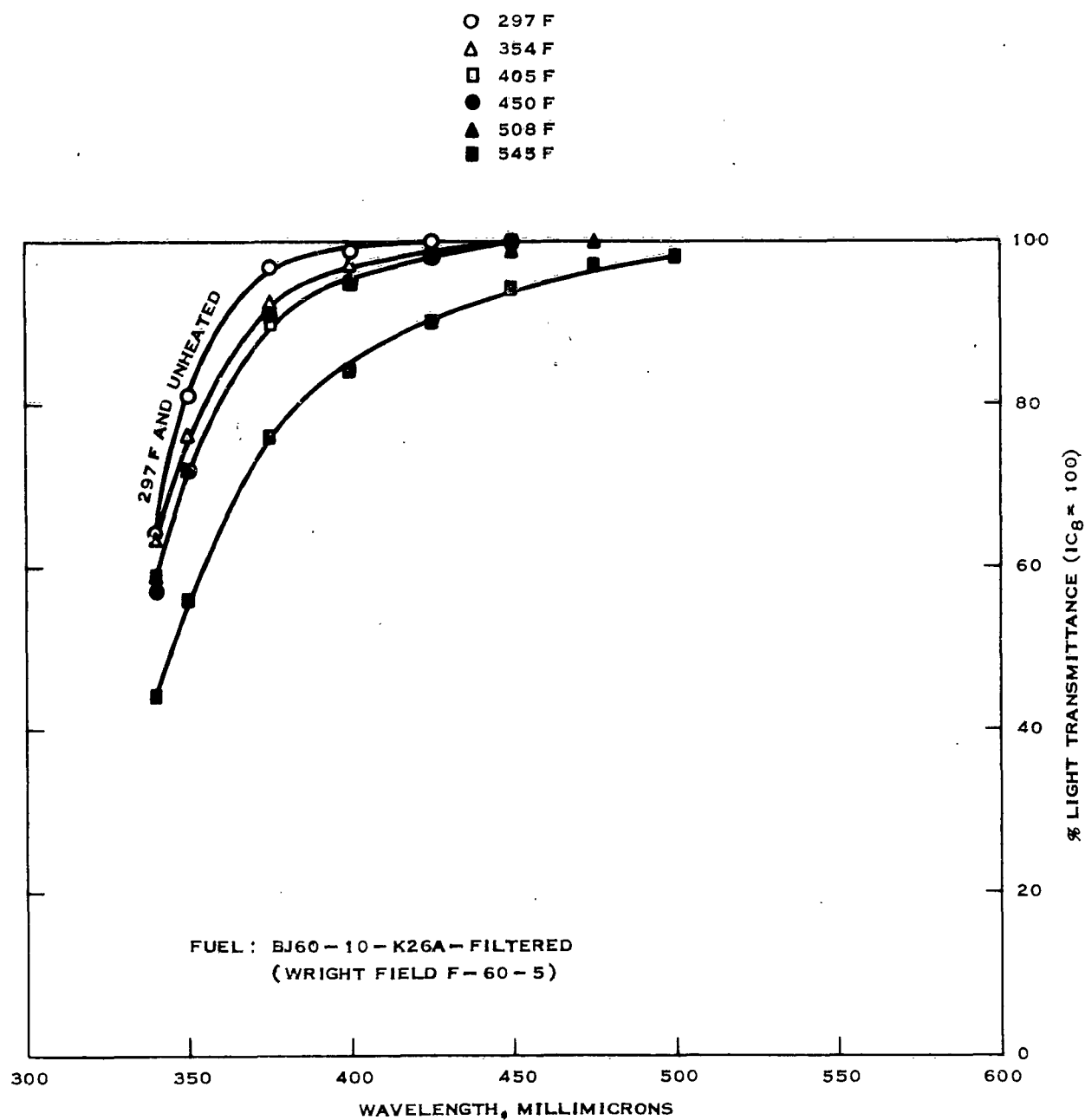
FIGURE 16
EFFECTS OF 20 MINUTE HEATING CYCLES IN THE 5 ML THERMAL
STABILITY BOMB ON LIGHT TRANSMITTANCE THROUGH JET FUELS

35
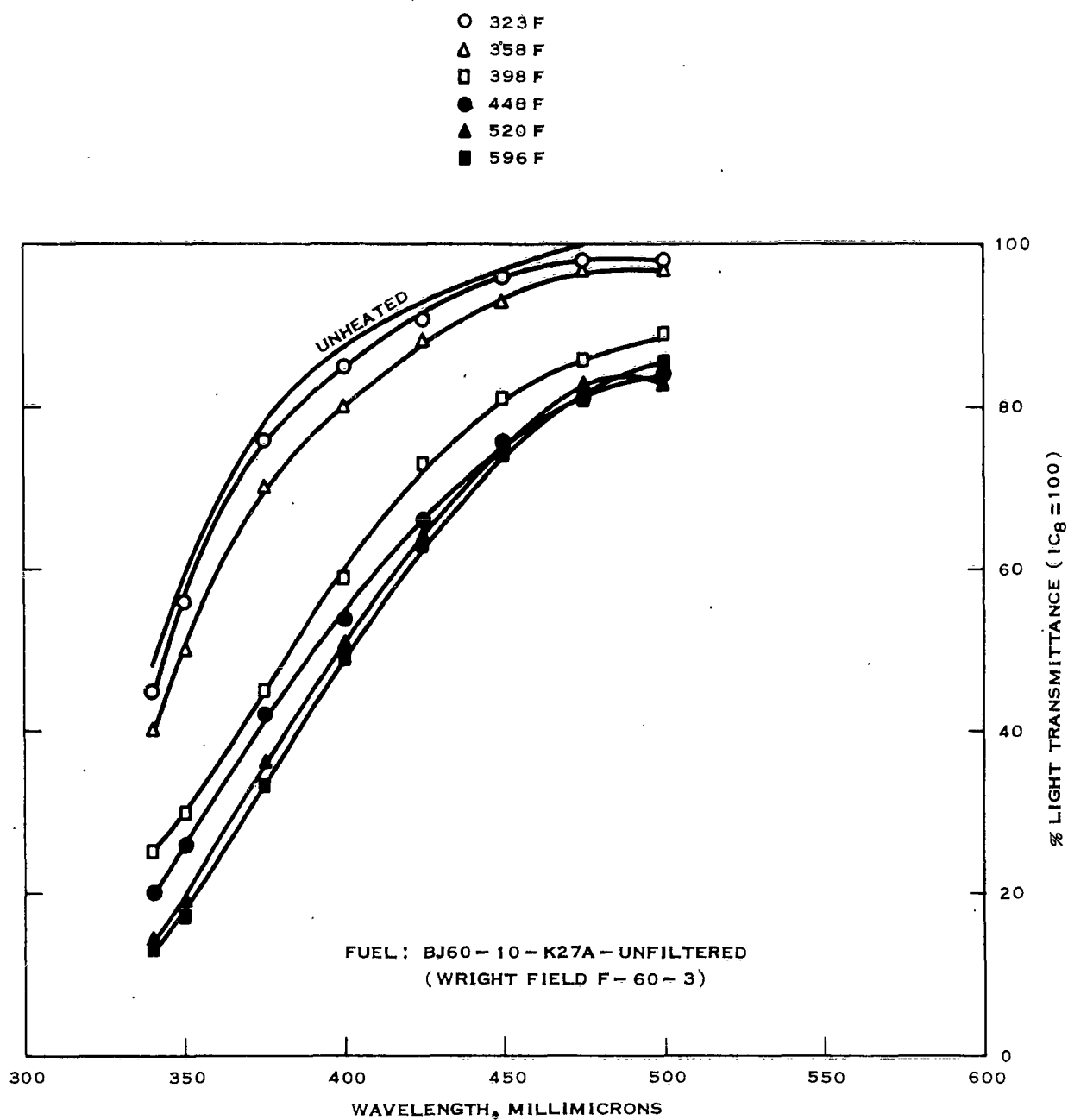
FIGURE 17
EFFECTS OF 20 MINUTE HEATING CYCLES IN THE 5 ML THERMAL
STABILITY BOMB ON LIGHT TRANSMITTANCE THROUGH JET FUELS
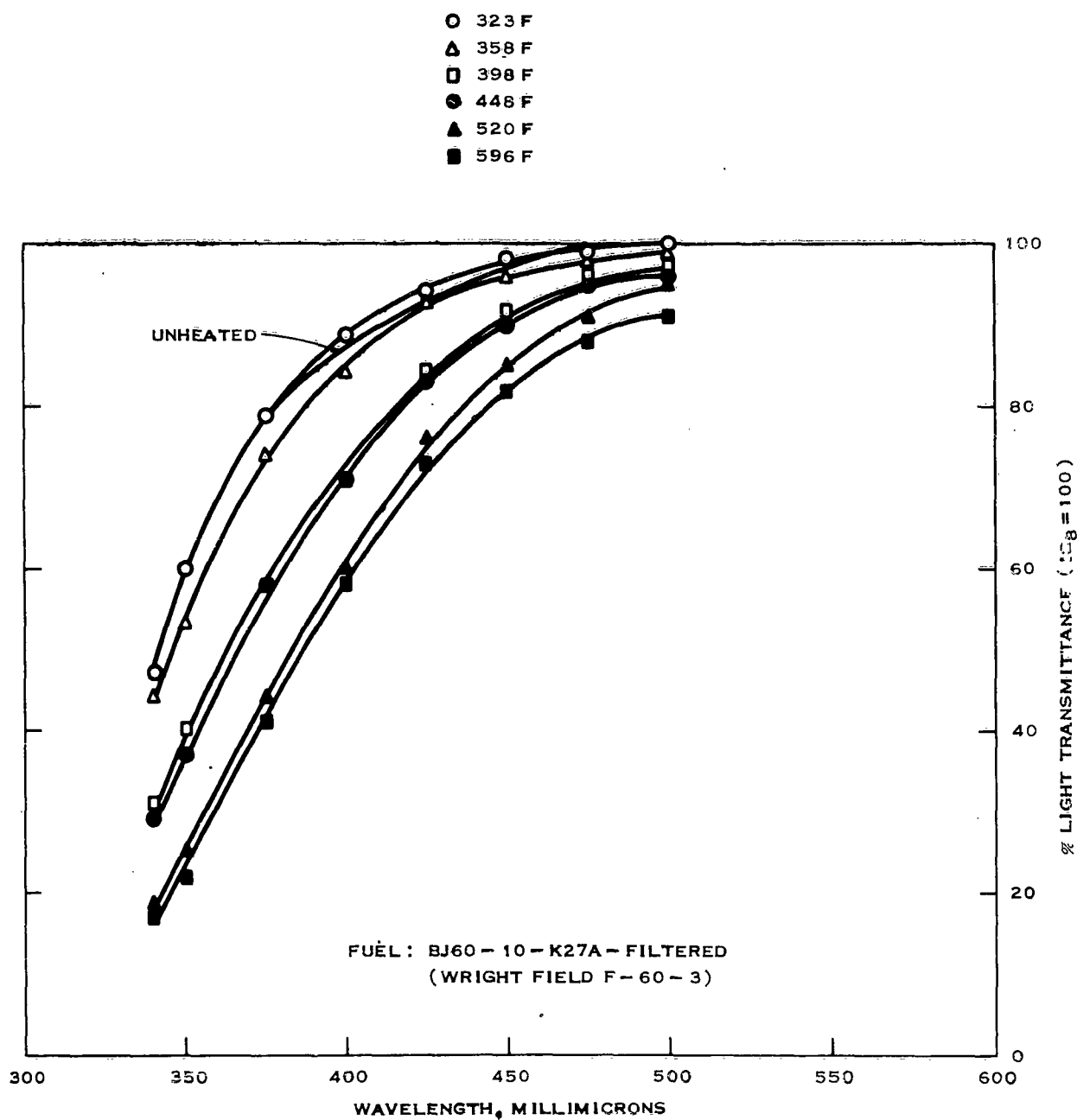
FIGURE 18
EFFECTS OF 20 MINUTE HEATING CYCLES IN THE 5 ML THERMAL
STABILITY BOMB ON LIGHT TRANSMITTANCE THROUGH JET FUELS

37
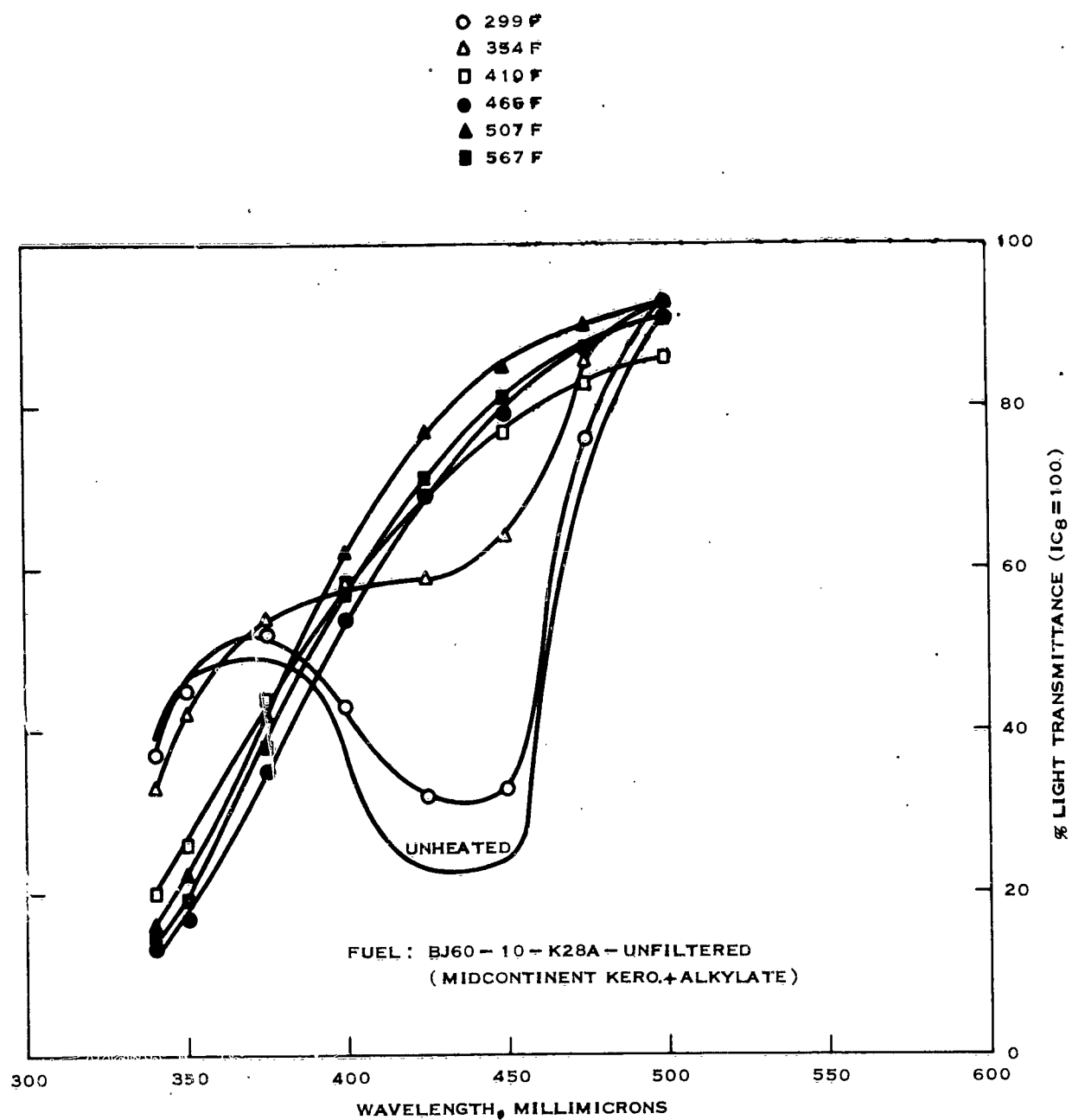
FIGURE 19

EFFECTS OF 20 MINUTE HEATING CYCLES IN THE 5 ML THERMAL
STABILITY BOMB ON LIGHT TRANSMITTANCE THROUGH JET FUELS

38
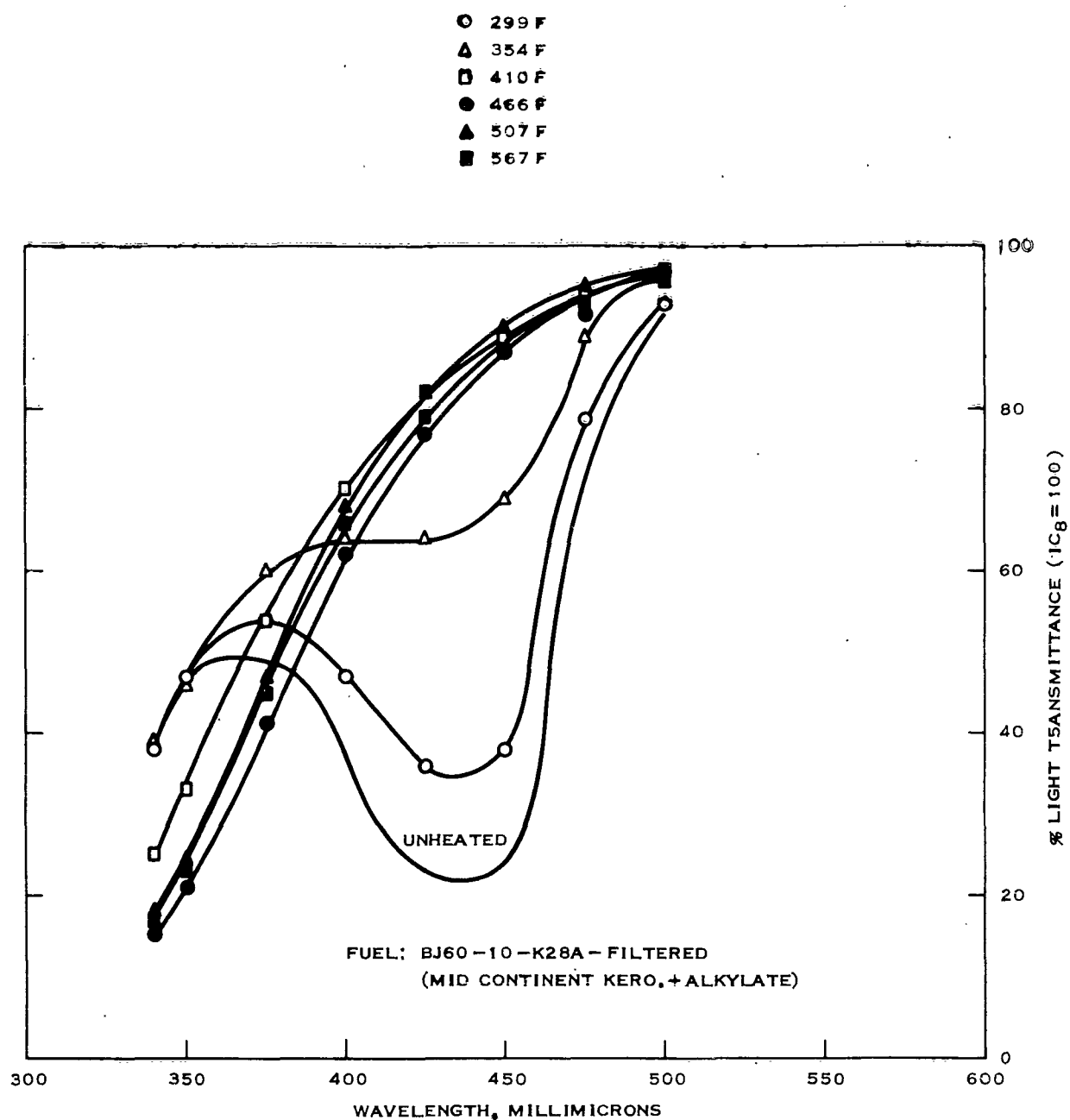
FIGURE 20
EFFECTS OF 20 MINUTE HEATING CYCLES IN THE 5 ML THERMAL
STABILITY BOMB ON LIGHT TRANSMITTANCE THROUGH JET FUELS

39
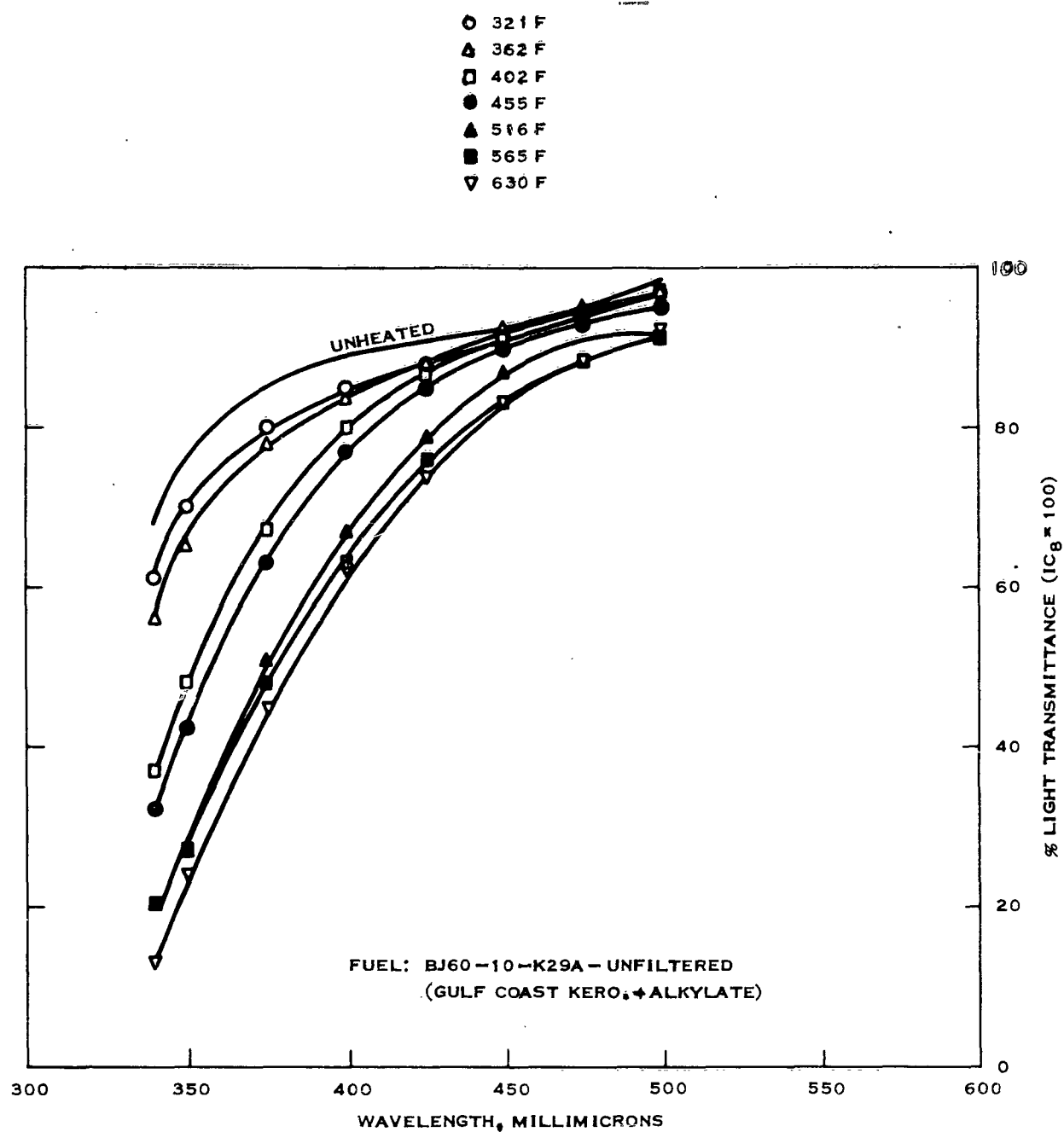
FIGURE 21
EFFECTS OF 20 MINUTE HEATING CYCLES IN THE 5 ML THERMAL
STABILITY BOMB ON LIGHT TRANSMITTANCE THROUGH JET FUELS

40
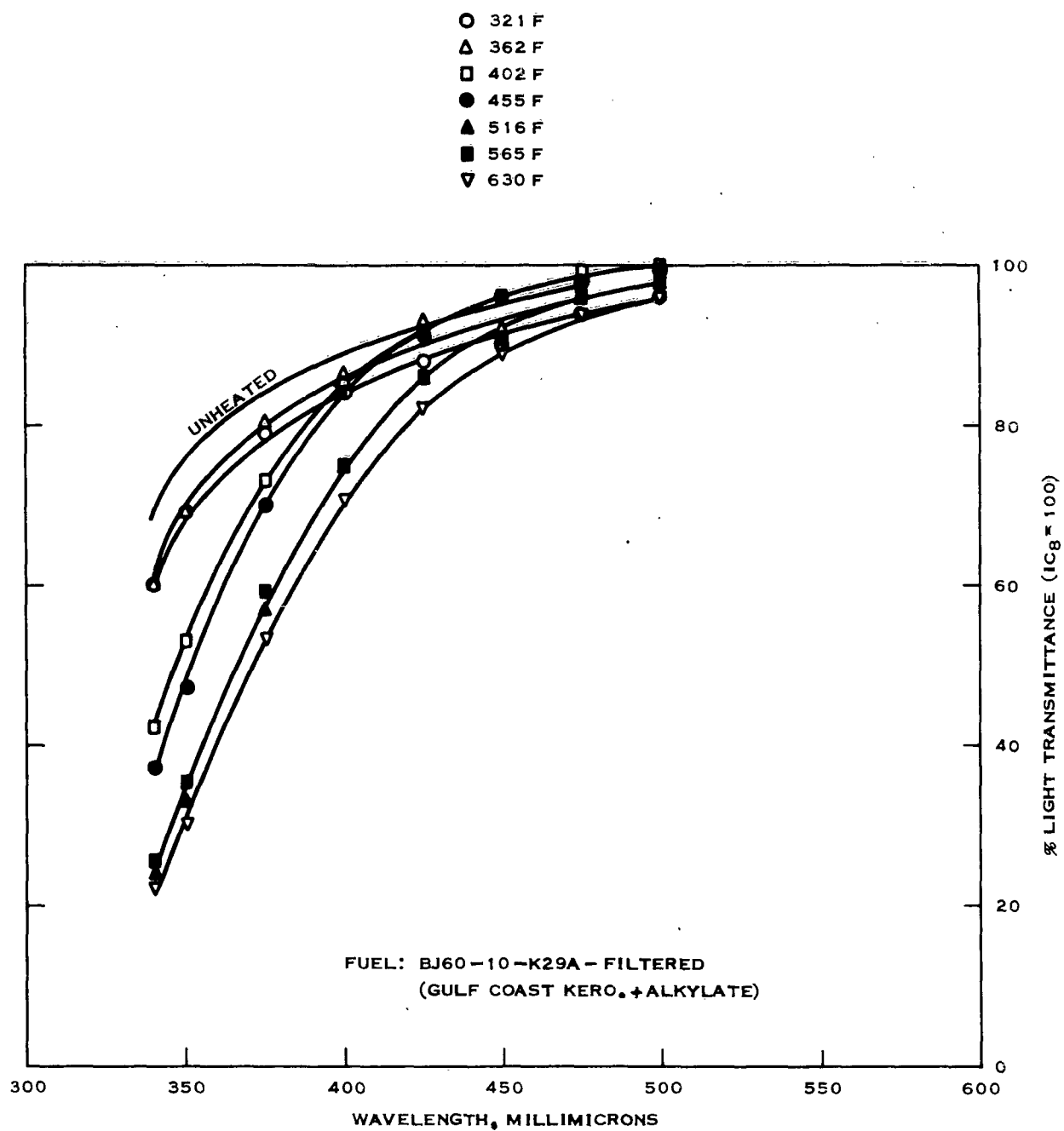
FIGURE 22
EFFECTS OF 20 MINUTE HEATING CYCLES IN THE 5 ML THERMAL
STABILITY BOMB ON LIGHT TRANSMITTANCE THROUGH JET FUELS

41
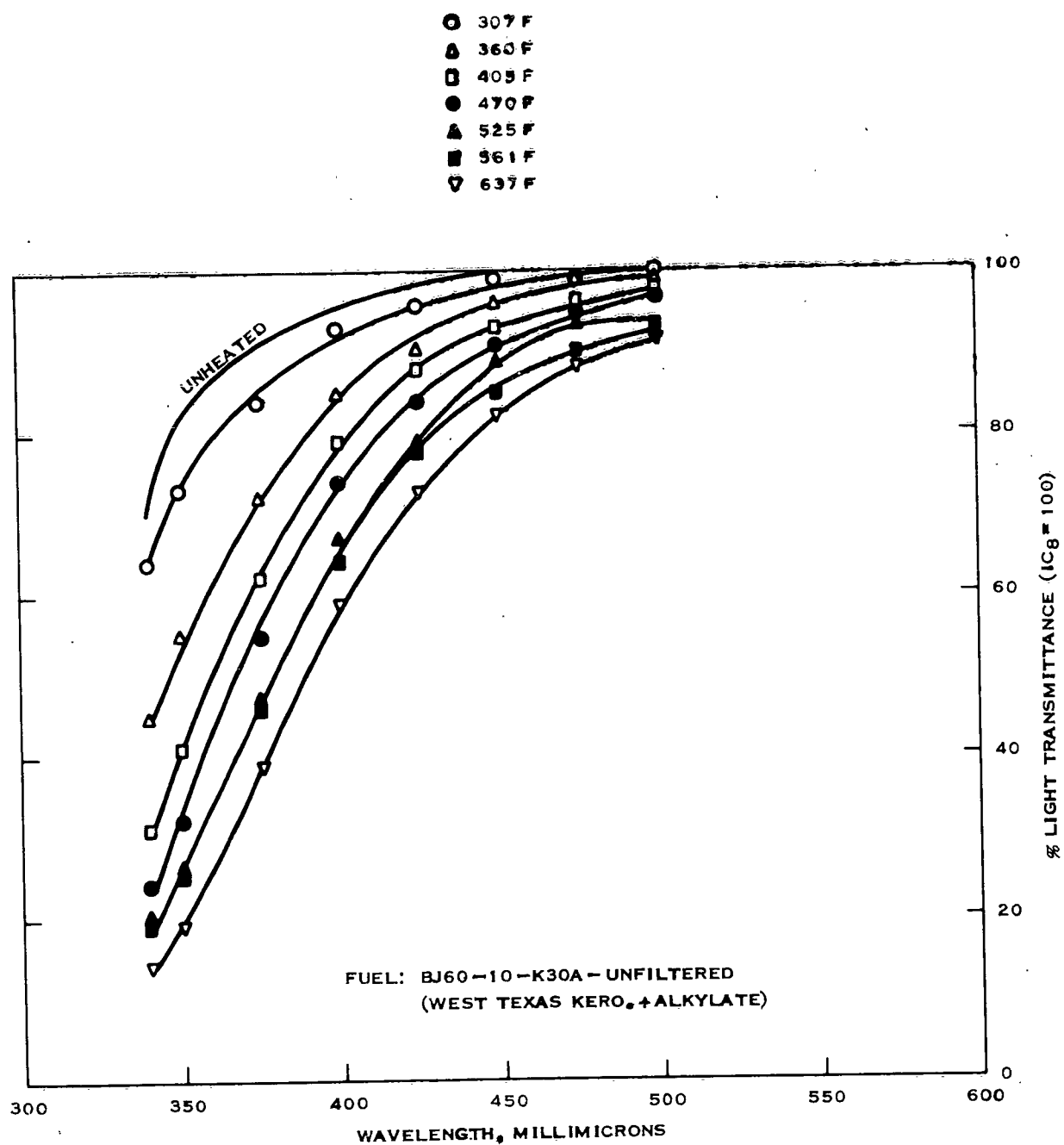
FIGURE 23
EFFECTS OF 20 MINUTE HEATING CYCLES IN THE 5 ML THERMAL
STABILITY BOMB ON LIGHT TRANSMITTANCE THROUGH JET FUELS

42
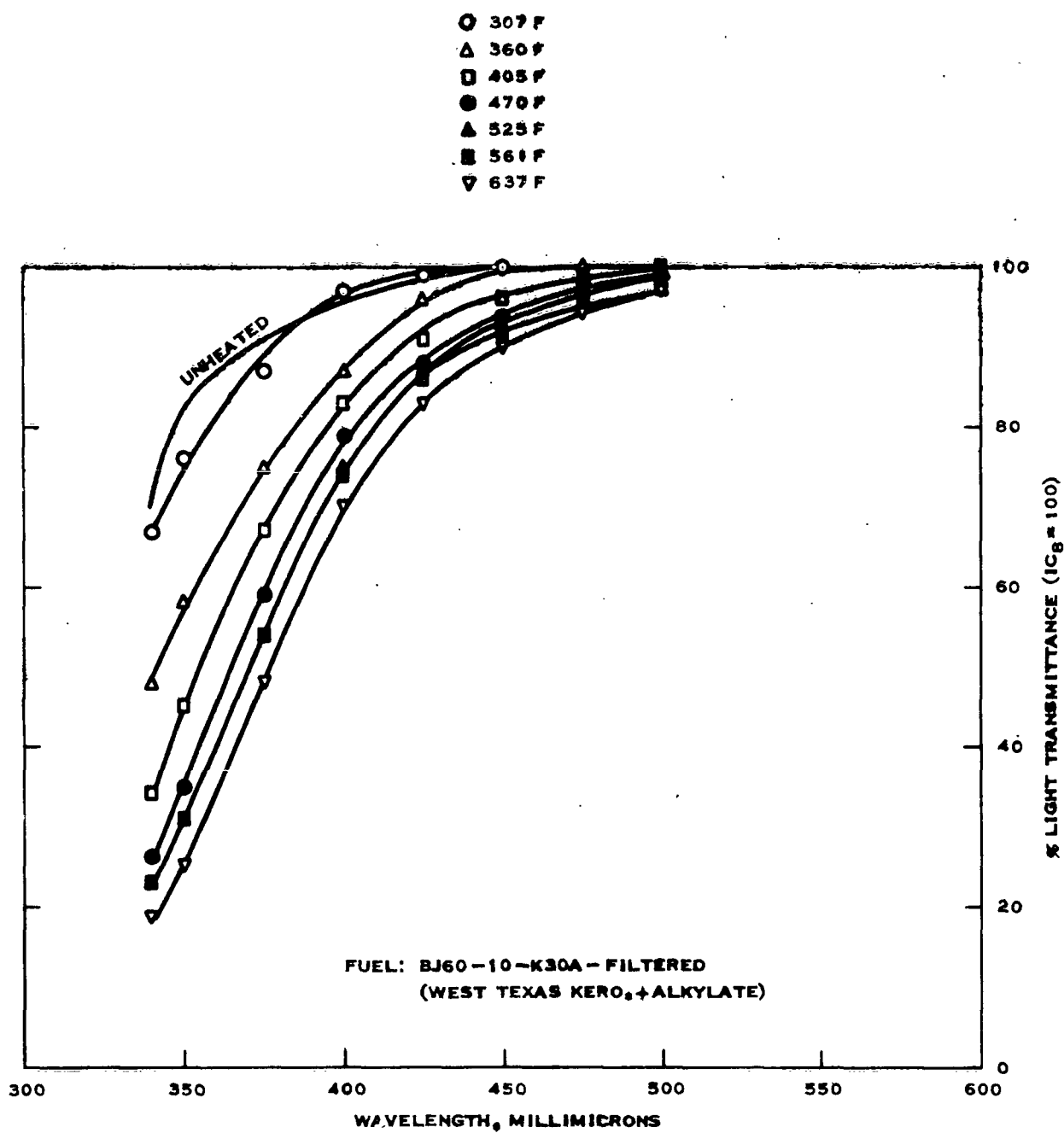
FIGURE 24
EFFECTS OF 20 MINUTE HEATING CYCLES IN THE 5 ML THERMAL
STABILITY BOMB ON LIGHT TRANSMITTANCE THROUGH JET FUELS

43
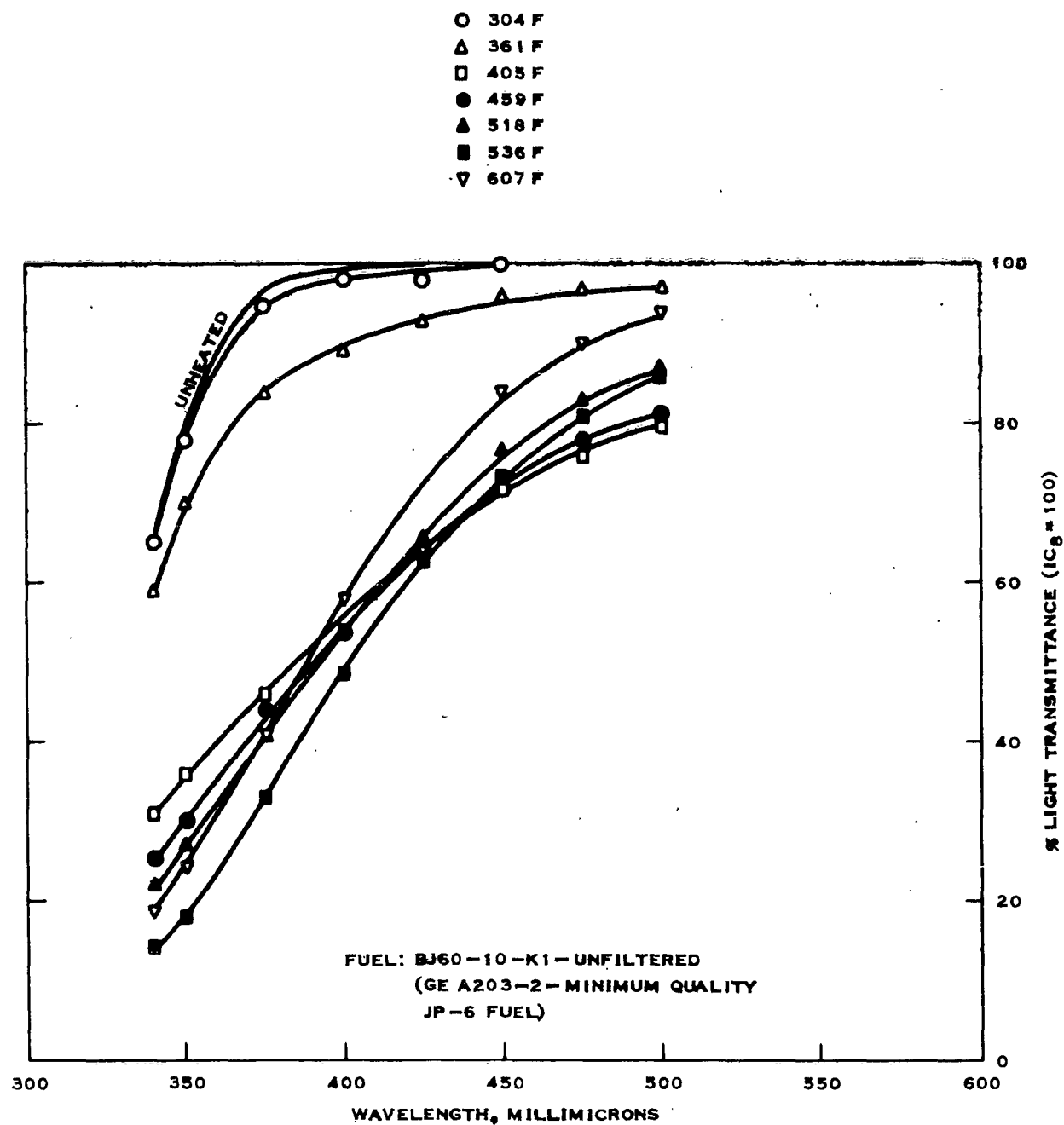
FIGURE 25
EFFECTS OF 20 MINUTE HEATING CYCLES IN THE 5 ML THERMAL
STABILITY BOMB ON LIGHT TRANSMITTANCE THROUGH JET FUELS

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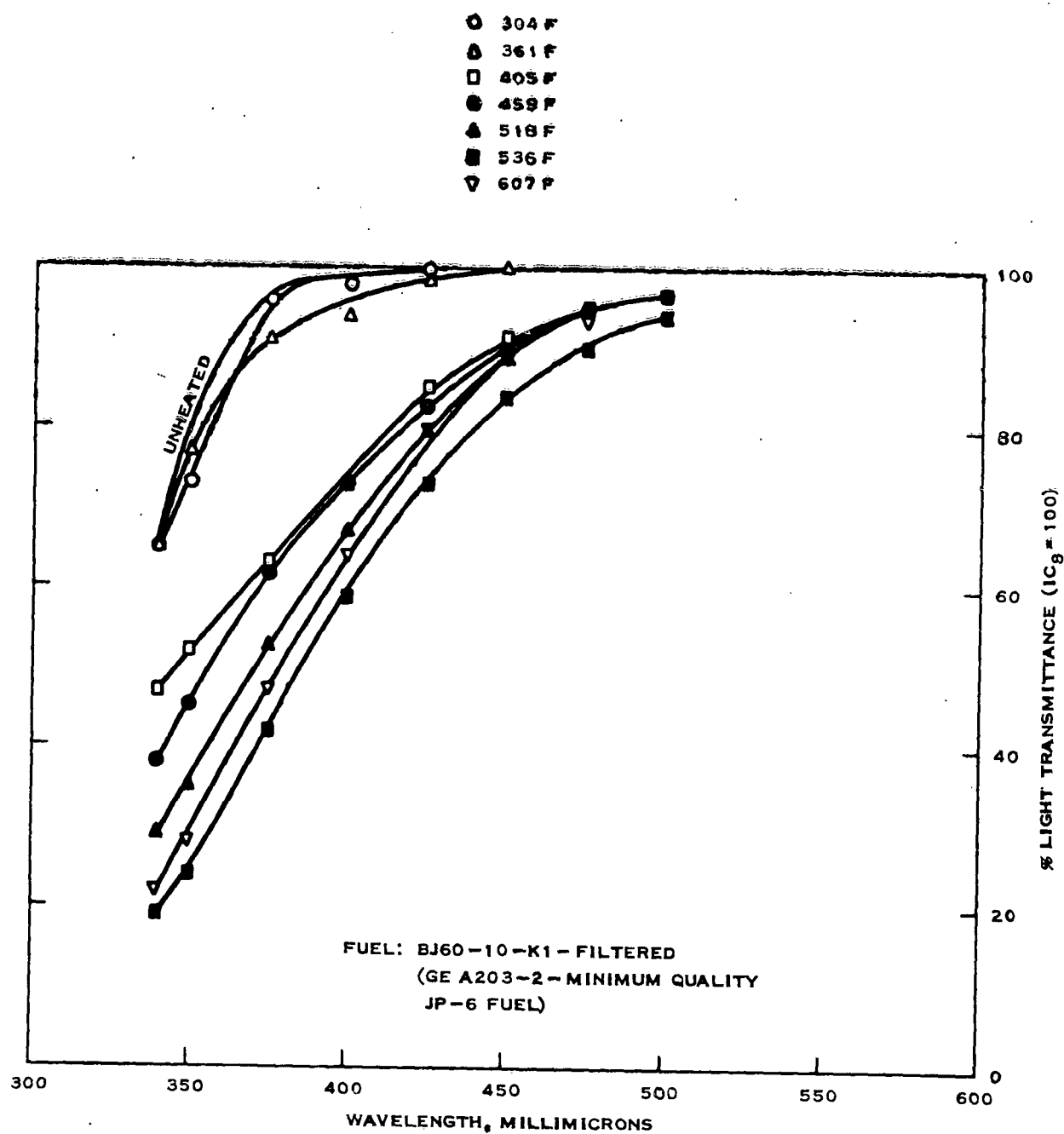
FIGURE 26
EFFECTS OF 20 MINUTE HEATING CYCLES IN THE 5 ML THERMAL
STABILITY BOMB ON LIGHT TRANSMITTANCE THROUGH JET FUELS

FIGURE 27
EFFECTS OF FILTRATION THROUGH 0.45 MICRON MILLIPORE PAPER ON
LIGHT TRANSMITTANCE THROUGH JET FUELS AFTER HEATING IN THE 5 ML
THERMAL STABILITY BOMB

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light transmission (at 350 millimicrons) after heating versus the temperature to which they were heated. It should be pointed out, however, that this can be done in two ways; (1) using the light transmittance as referred to some constant standard such as isooctane (used in these tests) or (2) using the transmittance as referred to the original or unheated transmittance of each fuel (i.e., transmittance as per cent of original transmittance). Using the former method, as shown in Figure 28, the fuel well established as the superior performer in the CFR Fuel Coker, BJ60-10-K26A (Wright Field F60-5), was also found to be superior by the 5 cc bomb-transmittance technique when plotted in this way. Similarly, fuel BJ60-10-K28A (Wright Field F60-3) which was the poorest performer in the Coker was also poorest by the light transmittance method. Fuels BJ60-10-K27A, K29A and K30A were observed to be of intermediate performance, as in the Fuel Coker, and of roughly comparable performance relative to each other. Although the Coker did manage to show some separation of performance of K27A, K29A and K30A the degree was not great and the fact that there is not complete agreement in the order of these three fuels when tested in the 5 cc bomb does not seem to detract greatly from these results. It was considered of interest to include in these tests a JP-6 fuel obtained from General Electric Company which has been found to be of marginal performance with respect to full-scale heat exchanger fouling tests (based on actual measurements of loss of coefficient of convective heat transfer, not visual rating methods) conducted in the General Electric Laboratories. The performance level of this fuel by the 5 cc bomb-light transmittance technique, shown also in Figure 28, seems completely reasonable in light of the known performance of the fuel. Included also on this plot are data obtained on a JP-5 type isoparaffinic alkylate fuel of well-known high stability. This fuel was also used to check out the warm-up characteristics of the system. Although the alkylate started out (300 F) with a rather low transmittance as compared to the stable JP-6 fuels, it changed relatively little with increasing temperature, as would be expected for a fuel of good stability. The rather low initial transmittance observed for this fuel is perhaps reasonable for the JP-5 volatility class fuels. Thus, on the basis of these raw transmittance plots the 5 cc bomb-light transmittance method looks rather promising in that it is sensitive to temperature changes and also shows some capability for broadly separating fuels in an order comparable to that obtained by CFR Fuel Coker tests.

A seemingly more logical way of considering these data is the second method cited above where the transmittance of the heated samples of each fuel is referred to the original or unheated transmittance of that fuel. This has been done in Figure 29, a plot of transmittance as a percentage of the original versus fuel temperature. In other words, this plot emphasizes changes induced by heating by normalizing them about the original fuel transmittance. This has the effect of disregarding original transmittance level (which may or may not be desirable). Considering Figure 29 it is immediately obvious that this method of plotting the data has altered the position of the K28A curve (poorest fuel in the CFR Coker) relative to K27A, K29A and K30A making it appear to be better at temperatures above 450 F than these fuels. The best fuel in the Coker, K26A, is again best in the 5 cc bomb, when plotted this way and the alkylate fuel only slightly less stable than K26A, which seems to fit prior knowledge of the performance of this fuel somewhat better. On this basis, too, K27A and K30A performed very much the same above 400 F while K29A tended to appear slightly more stable between 400 F and 500 F. Above 500 F, however, K27A, K29A, K30A and K1 were much the same.

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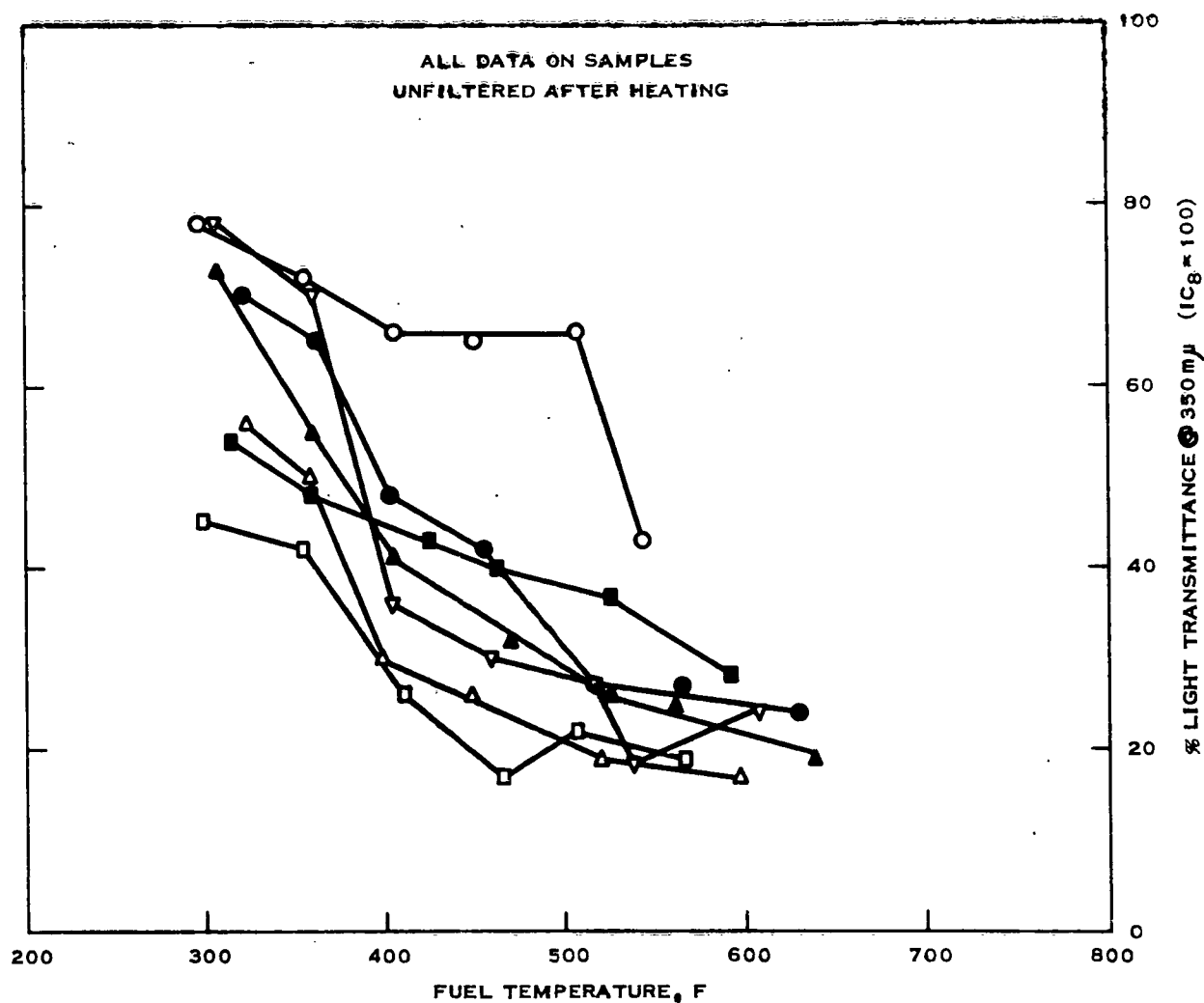
FIGURE 29
RELATIONSHIP BETWEEN TEST TEMPERATURE AND LIGHT TRANSMITTANCE FOR
FUELS AFTER HEATING IN THE 5 ML THERMAL STABILITY BOMB

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Actually, then, plotting of the light transmittance data in terms of percentage of original transmittance tended to yield curves showing sharp temperature responses but which separated the fuels only into groups of very stable fuels and marginally stable fuels. In general, the agreement with Fuel Coker data is poorer when the data is plotted in this way, although this is not necessarily a good criterion for deciding whether the technique is good or bad.

With these light transmittance data available it was, of course, of interest to consider their possible correlation, or lack of it, with CFR Fuel Coker data. Inspection of the curves shown in Figures 28 and 29 indicated that maximum separation of fuels occurred in the range 400 F to 500 F in the 5 ml bomb test, so the data obtained at 450 F fuel temperature was selected as offering the best possibility for correlation with Coker data. Again, as in Figures 28 and 29, the transmittance data was considered both in terms of isooctane as the standard ($iC_8 = 100$) and in terms of the unheated test fuel as the standard (unheated fuel = 100). Plots of these data versus CFR Fuel Coker filter merit rating obtained at 425/525 F are shown in Figure 30, from which it will be seen that a more than coincidental relationship appears to exist and this trend is most definite when the data are considered on the basis of the unheated test fuel as the standard.

While the correlation of light transmittance with filter merit rating seems promising, the same is not true for correlation with Coker preheater tube color ratings, as may be seen from Figure 31. It is obvious upon inspection of this plot that no correlation whatsoever exists. Little more can be said except that this may possibly be a result of either the insensitivity of the Coker preheater rating method or the possibility that the optical technique predicts only precursors of non-adhesive particulate matter formation while ignoring precursors of adhesive deposits of the type causing preheater fouling.

Summarizing the information gathered thus far with regard to the 5 ml bomb-light transmittance technique it appears that:

1. A definite sensitivity with respect to fuel temperature has been demonstrated.

2. The method is able to separate fuels into categories of good, intermediate and bad. At this stage of development the method does not appear able to make finer distinctions.

3. Correlation of light transmittance data with CFR Fuel Coker filter merit rating is promising, but no correlation was found to exist with Coker preheater color ratings.

4. The technique is rapid, thrifty of sample size and requires only simple equipment. These factors coupled with indications of promising data make further study and refinement seem desirable.

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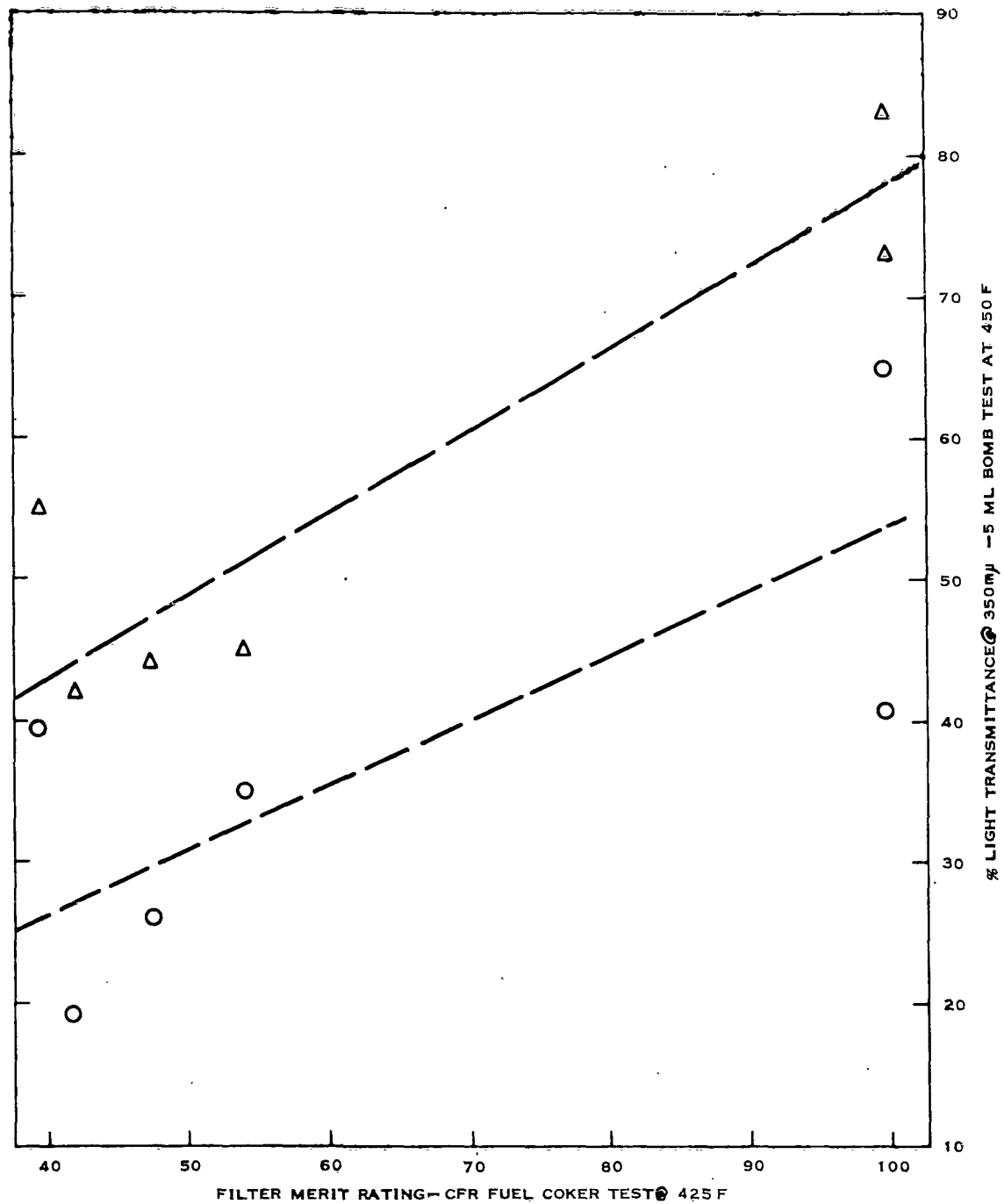
FIGURE 30
RELATIONSHIP BETWEEN THERMAL STABILITY RATINGS IN TWO
TYPES OF APPARATUS USING JP-5 AND JP-6 FUELS
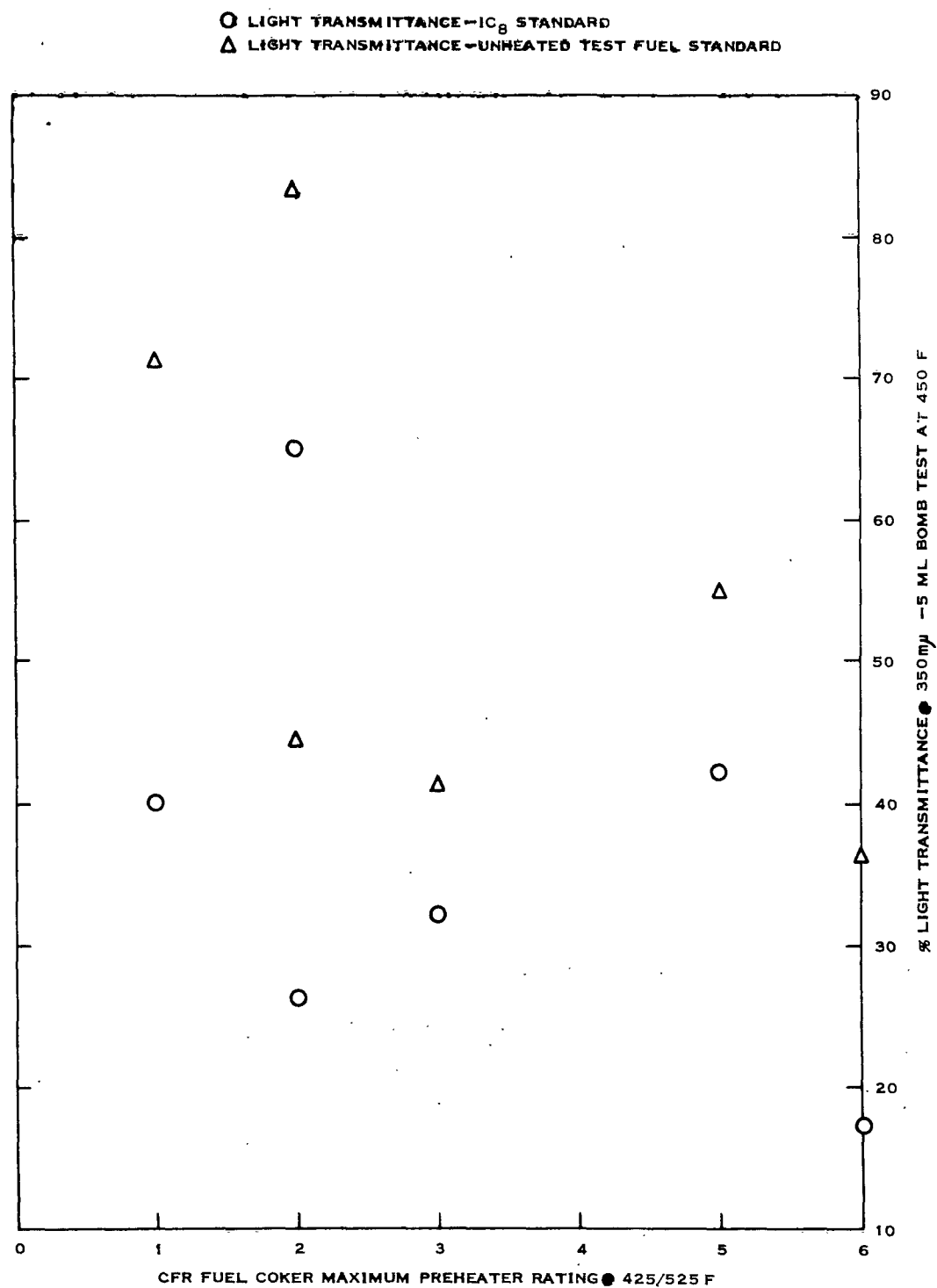
FIGURE 31
RELATIONSHIP BETWEEN THERMAL STABILITY RATINGS IN TWO TYPES OF
APPARATUS USING JP-5 AND JP-6 FUELS.

III. STORAGE STABILITY OF JP-6 TYPE JET FUELS

At the beginning of this project JP-6 grade jet fuels were required by specification to pass the CFR Fuel Coker thermal stability test at 400-500 F temperature conditions. It had been observed at Wright Field that certain products meeting the JP-6 specification in this respect when fresh, deteriorated when stored for periods of several months in vented tanks before being used. Objectives of the present research are to reproduce these thermal stability quality changes under controlled storage conditions and to relate them by chemical analysis to specific types of fuel components or contaminants.

Considerable past work on jet fuel storage stability has been carried out under military sponsorship. However much of this work has dealt with storage instability in terms of increases in gum content instead of high temperature stability performance in the CFR Coker apparatus. The types of jet fuels studied have been limited to JP-3, 4 and 5's, which are required to pass the CFR Coker test only at 300-400 F temperature conditions -- a much less stringent requirement than must be met by JP-6. Therefore, storage instability manifested in JP-6 products by poorer CFR Fuel Coker performance at 400-500 F temperature conditions may involve different types of reacting materials than those responsible for thermal instability effects at the milder conditions involved in the other specifications.

It was therefore planned to examine the changes under controlled storage conditions of a series of JP-6 grade jet fuels selected to provide variations in composition and fresh condition thermal stability ratings, with the following specific objectives:

1. To establish the magnitude of change in CFR Coker performance ratings and related properties following storage at 110 F hot room conditions for six months time or more and at ambient temperatures for one year.

2. To evaluate the role of oxygen availability in such thermal stability losses by means of storage in both sealed and vented containers, and with selected antioxidant fuel additives.

3. To correlate the changes in stability performance after storage with fuel composition changes determined by various chemical analyses, to make possible recommending preventative measures.

4. To provide data from which an accelerated method can be developed for predicting fuel deterioration in terms of thermal stability quality in storage.

The present report discusses results through only the six months 110 F hot room phase of the program.

A. Test Program

A series of five JP-6 fuel blends were selected to provide variations in geographical source and in thermal stability quality at the start of the controlled storage period. Two of the fuels were furnished by WADD and the remaining three

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were blended for this project by Phillips. These fuels were stored in 15 gallon, uncoated, steel drums at a constant temperature of 110 F in the hot room. With each fuel four separate drum samples were stored, two of which were sealed under a dry, nitrogen atmosphere while the remaining two were vented, water saturated and aerated at monthly intervals throughout the storage period. Comparisons between the two groups of samples were expected to indicate the influence of gross oxygen availability on deterioration in CFR Fuel Coker ratings. To explore the possibility of neutralizing oxygen effects, samples of one of the poorer test fuels were stored in the presence of five different antioxidant-type fuel additives -- in vented drums only, to allow unlimited access to oxygen.

As to duration, six months was the basic storage period for the hot room samples -- with the option that if CFR Coker results with the first 15-gallon drum of each fuel removed from the hot room at this time show no evidence of deteriorating quality, the second drum was to be left in for another three months time. In addition, small samples were removed from the vented drums for selected chemical analyses at two and four months time.

The results of controlled constant temperature hot room storage are to be supplemented by ambient temperature storage for one year's time, using 55-gallon drums as vented containers and 15-gallon drums as sealed containers. Here normal breathing due to day-to-day temperature variations is relied upon to maintain oxygen saturation of the vented samples, though they were artificially water saturated and aerated when placed in storage.

The drums used as storage containers were purchased new at the start of the program and carefully rinsed to assure constant internal surface conditions. The possibility of corrosion of the drums during storage was followed by comparing Millipore particulate contamination tests on the fresh and stored fuel samples, supplemented by analyses for soluble iron and copper.

Four CFR Fuel Coker tests were run on each fuel when fresh, to establish the base line thermal stability quality level as accurately as possible. Duplicate tests were made at the (then) specification temperature level of 400-500 F, while the other two tests were made at 425-525 F and 450-550 F temperature conditions respectively to establish actual threshold failure levels. Following six months storage at 110 F, duplicate tests were run on each fuel at temperature conditions just below the fresh condition threshold failure level using one of the two 15-gallon storage samples. If these tests were not greatly different in rating from the fresh condition rating at the same temperature, the second 15-gallon sample was left in storage for an additional three months time. If the first two tests showed appreciably poorer ratings however, the second 15-gallon sample was removed from storage and two additional tests were run at temperatures chosen to define a new threshold failure level following storage -- providing three point temperature-versus-CFR Coker rating curves for comparison against the fresh condition curves so as to put the final judgement as to whether the fuels had deteriorated in thermal stability during storage on as firm a basis as possible. All CFR Fuel Coker tests were run under completely standard conditions, (D 1660-59T), except that a filter by-passing system was employed whenever a ΔP of 25 inches Hg was reached, so as to place all preheater ratings on a five hour basis. A single operator and test apparatus were employed for every CFR Fuel Coker test

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carried out as a part of this program, to minimize operator and equipment variables affecting test repeatability.

A wide variety of chemical analyses were made on these fuels, for comparison with the present JP-6 fuel specification and to establish baseline characteristics against which to compare changes in thermal stability quality after storage. Many of these analyses were repeated periodically as the storage period progressed in an attempt to follow chemical changes taking place which might be responsible for CFR Coker performance changes.

Table IV summarizes pertinent features regarding the storage variables, while Table V lists the various chemical analyses and other test work done before and after storage.

The drum coating material mentioned in Table IV (EC776SR) is used for sealing wing tanks in certain military aircraft, and was included in the present program to indicate whether any effects on fuel thermal stability performance might be expected due to exposure to such materials in the aircraft.

The chemical analysis schedule outlined in Table V was the product of discussions with Phillips Analysis Branch and Wright Field representatives to begin with, and has been liberally revised and supplemented as the storage period progressed, to provide a broad background of supporting information about these storage fuels against which to compare their relative tendencies to deteriorate in thermal stability rating after storage. Considerable attention was given to trace non-hydrocarbon constituents of these fuels, both organic and inorganic, in the selection of the analyses to be made. Note that a number of these analyses were made both before and after the fuels had been subjected to CFR Fuel Coker testing, in an attempt to indicate which fuel constituents disappeared in the course of making the deposits.

This program was planned around JP-6 test fuels with thermal stability in the fresh state ranging from good to intermediate to marginal. Two of the fuels were supplied by Wright Field and turned out to be quite good in thermal stability performance. Therefore the other three fuels were blended by Phillips to fall more-or-less in the intermediate and marginal thermal stability categories (considered in terms of threshold failure temperature level). To provide variations in refinery stocks, the fuels were blended using Midcontinent, Gulf Coast and West Texas kerosines respectively as major components. A 290-390 F alkylate and a 350-550 F alkylate were used as blending components in upgrading all three of these kerosines to meet JP-6 distillation and thermal stability requirements. The alkylate components in these blends also improved freezing characteristics -- however, it was found that the proportions of total alkylate in all three kerosines resulting in the desired thermal stability performance were insufficient to produce freeze points quite meeting JP-6 limits (-65 F) so this was sacrificed in order to maintain thermal stability at the intermediate to marginal quality level for the purposes of the present program. Final compositions of the test fuels as stored are given in Table VI. It was necessary to blend the West Texas fuel in two batches because of blending tank size limitations. These batches differed significantly in thermal stability ratings. The cause for this is believed due to differences in trace constituents among the individual drums of the kerosine used. Therefore these two batches were treated as separate fuels from this point on. The batch with the poorer rating (K500) was chosen for the

TABLE IV

OUTLINE OF PROGRAM TO STUDY EFFECTS OF

STORAGE ON JP-6 JET FUEL THERMAL STABILITY

I. Procedures

A. Storage Conditions – 6 and 9 months in 110 F Hot Room, one year at ambient temperatures.

B. Both vented and sealed containers used for base fuels – vented only for antioxidant blends.

C. All vented samples saturated with both air and water at start of program – hot room vented samples only aerated at monthly intervals thereafter.

D. Sealed samples stored dry under nitrogen.

E. 8 one-pint samples of each fresh fuel stored under nitrogen at 30-40 F for use in supplementary chemical analysis work after storage.

F. Individual storage samples 13 1/2 gallons in size at all but vented ambient temperature conditions, which are 45 gallons.

G. New, uncoated, 19 gauge steel drums, 15 and 55 gallon sizes, used as sample containers.

H. All drums stored upright with about 20 per cent outage.

I. Vents assembled from mild steel pipe fittings.

J. One fuel stored additionally in vented drums coated with MMM-EC776SR.

K. Test fuels selected to vary in "fresh" thermal stability quality and in composition.

TABLE I

TESTING AND CHEMICAL ANALYSIS SCHEDULE FOR JP-6 STORAGE SAMPLES

Test Method	Fresh	Vented Container Storage					Sealed Container Storage		
		8 Weeks 110F	16 Weeks 110F	26 Weeks 110F	39 Weeks(4) 110F	52 Weeks Ambient	26 Weeks 110F	39 Weeks(4) 110F	52 Weeks Ambient
JP-6 Specification Tests									
Distillation (D86-59)	x			x	x	x	x	x	x
Gravity (D287-55)	x			x	x	x	x	x	x
Existent Gum (D381-58T)	x			x	x	x	x	x	x
Potential Gum (D873-57T)	x								
Total Sulfur (D1266-59T) (1)	x			x	x	x	x	x	x
Mercaptan Sulfur (D1219-56) (1)	x								
Freeze Point (D1477-57T)	x								
Heating Value (D240-57T)	x								
Kinematic Viscosity (D445-53T)	x								
Aromatics (D1319-58T)	x								
Olefins (D1319-58T)	x								
Smoke Point (D1322-59T)	x								
Corrosion (D130-56)	x			x	x	x	x	x	x
Water Reaction (D1094-57)	x			x	x	x	x	x	x
Flash Point (D93-58T)	x								
Aniline Point (D611-55T)	x								
Thermal Stability (D1660-59T)	x			x	x	x	x	x	x
Special Tests									
Water Content (Karl Fisher)	x	x		x	x	x	x	x	x
Particulate Matter (Millipore Filtration)	x	x	x	x	x	x	x	x	x
Saybolt Color (D156-53T) (1)(3)	x	x	x	x	x	x	x	x	x
Total Oxygen (Direct Combustion Plus Gas Chromatography) (1)	x			x	x	x	x	x	x
Peroxide No. (Arsenite Method) (1)	x	x		x	x	x	x	x	x
Neutralization No. (D664-58) (1)	x	x		x	x	x	x	x	x
Total Nitrogen (Kjeldahl on Sulfuric Acid Extract) (1)	x					x			x
Pyrrole Nitrogen (See Footnote 5)	x	x		x	x	x	x	x	x
Basic Nitrogen (Perchloric Acid Titration) (1)	x	x		x	x	x	x	x	x
Polycyclic Aromatics (UV Spectroscopy) (1)	x			x	x	x	x	x	x
Gas Chromatography (Technique Varied to Suit Sample) (1)	x			x	x	x	x	x	x
Soluble Copper (Neocuproine-Spectrophotometric)	x			x	x	x	x	x	x
Soluble Iron (O-Phenanthroline Color Indicator on Hydrochloric Acid Extract)	x			x	x	x	x	x	x
Bromine Number (Coulometric Method) (1)	x			x	x	x	x	x	x
Soluble Lead (Dithizone Extraction)	x								

(1) Before and after thermal stability tests at "failure" conditions
(2) At 400-500F conditions and other temperatures as necessary to establish "failure" conditions
(3) Before and after 3.0 micron filtration
(4) 39 Week tests only if no thermal stability changes at 24 weeks
(5) Journal of Analytical Chemistry 30, 259, 1958

TABLE VI

COMPOSITION OF JP-6 STORAGE FUELS

Fuel Ident. BJ60-10-	Description	Kerosine	Composition, Wt, %	
			350-550 F Alkylate	290-390 F Alkylate
K26	WPAFB, F-60-5	—	—	—
K28	Blend (300 Gallons)	75 Midcontinent	10	15
K29	Blend (300 Gallons)	65 Gulf Coast	—	35
K27	WPAFB, F-60-3	—	—	—
K30	Blend (300 Gallons)	60 West Texas	15	25
K500	Additive Base Fuel (500 Gallons)	60 West Texas	15	25
K31	Base + 0.05 Wt. % 2,6-di-tert-butyl-4-methyl phenol			
K32	Base + 0.01 Wt. % mixed C_{12}-C_{14} tert-alkyl primary amine			
K33	Base + 0.01 Wt. % experimental hindered phenol			
K34	Base + 0.05 Wt. % 2,2' methylene-bis-(4-methyl-6-tertiary butyl phenol)			
K35	Base + 0.10 Wt. % 4,4' methylene-bis-(2,6-di-tert-butyl phenol)			
K53	Fuel No. 3 (K29) Stored in drums coated inside with MMM-EC 776SR			

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additive evaluation work and the other (K30) was stored individually.

The five antioxidant additives being investigated have been chosen by agree-
ment with Wright Field, and are all commercially available materials. Actual
concentrations of each additive were established by running concentration versus
CFR Fuel Coker rating curves (see Figure 32), with the idea of picking a concentra-
tion improving CFR Coker performance of the fresh fuel and high enough to offer
promise of coping with oxygen taken up by the fuels during storage. All five
additives improved the filter plugging performance of this fuel to the passing
level. However with the mixed $C_{12}-C_{14}$ tert-alkyl primary amines preheater deposits
were not improved and in fact appeared to become worse with the higher concentra-
tions -- thus the lowest concentration tried with this additive was used in
storage samples.

A very useful reference aiding the selection of additives to be employed
in this program was a paper presented by Shell Development at the Fifth World
Petroleum Congress (20).

It was desired that each base fuel be reduced to initially low water contents
and be made as homogeneous as possible from drum to drum. The system shown in
Figure 33 was employed for this purpose, with all the drums for each test fuel
connected in a closed circuit and the fuel recirculated for 8 hours time at a rate
of one gallon per minute. Uniform dryness was achieved by including in the circuit
a two-inch diameter iron pipe two feet long packed with Linde 4A Type Molecular
Sieve, followed by two five-micron Purolator filters to prevent contamination by
molecular-sieve "fines" and to pick up other solids present in the fuels after
blending.

B. Characteristics of Test Fuels Before and After Storage

1. Thermal Stability Performance

Results of all thermal stability tests on the five non-additive JP-6 storage
fuels are listed in Table VII. and are shown plotted against test temperature in
Figures 34-38. Considering first the fresh condition ratings of these fuels, it
is shown that a range in quality was represented based on the JP-6 specification
allowable limits of 10 inches of Hg maximum in filter pressure drop and a "3"
maximum in preheater deposit color rating at 400-500 F temperature conditions.
Two of the fuels (K29 and 30) were borderline in quality by these criteria, one
(K28) easily passed at 400-500 F but failed at 425-525 F temperature conditions,
while the remaining two fuels (K26 and 27) easily passed both at 400-500 F and
425-525 F.

As to the effects of 26 weeks aging at 110 F, there was no particular re-
lationship shown between the fresh condition CFR Fuel Coker ratings of these fuels
and their relative tendencies to deteriorate in this respect during storage. Of
the two fuels best in rating to begin with, sample K26 showed no change in
performance during storage while sample K27 deteriorated significantly, particu-
larly in terms of filter plugging. Since fuel K27 was inadvertently contaminated
with Linde 4A molecular sieve fines when preparing it for storage, an extra test
was carried out in which the normal prefiltration procedure with 3.0 micron
Whatman paper was followed up by two passes through 0.45 micron Millipore filter
paper -- to determine whether any of the molecular sieve material might not

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TABLE VII

THERMAL STABILITY OF JP-6 NONADDITIVE TEST FUELS

Fuel Identification BJ60-10-	Test Temperature Preheater	Test Temperature Filter	Tube Ratings 0	1	2	3	4	5	6	7	Max. Rating	Filter Merit Rating	Minutes to 25" Mg ΔP	ΔP in Hg. to 300 Minutes
K26-WADD (F-60-5)	400	500	7	6	0	0	0	-	-	-	1	87	>300	.07
Before Storage	400	500	8	3	2	0	0	-	-	-	2	82	>300	.15
	425	525	3	3	7	0	0	-	-	-	2	99	>300	.03
	450	550	6	1	2	2	2	-	-	-	4	29	>300	.01
After 26 wks. Sealed	425	525	6	3	4	0	0	0	0	0	2	99	>300	.00
Storage at 110 F	425	525	8	3	2	0	0	0	0	0	2	99	>300	.00
After 26 wks. Vented	425	525	8	3	2	0	0	0	0	0	2	99	>300	.00
Storage at 110 F	425	525	5	6	2	0	0	0	0	0	2	99	>300	.00
K27-WADD (F-60-3)	400	500	13	0	0	0	0	-	-	-	0	77	>300	.32
Before Storage	400	500	11	2	0	0	0	-	-	-	1	78	>300	.30
	425	525	9	4	0	0	0	-	-	-	1	65	>300	2.18
	450	550	8	1	0	0	4	-	-	-	4	69	>300	1.12
	450	550	8	0	0	0	5	-	-	-	4	56	>300	9.65
After 26 wks. Sealed	400	500	9	4	0	0	0	0	0	0	1	67	>300	1.53
Storage at 110 F	425	525	8	2	3	0	0	.0	0	0	2	47	241	>25
	425	525	6	6	1	0	0	0	0	0	2	48	258	>25
	450	550	9	0	1	0	2	1	0	0	4	43	170	>25
After 26 wks. Vented	400	500	8	5	0	0	0	0	0	0	1	54	>300	14.13
Storage at 110 F	425	525	9	1	1	2	0	0	0	0	3	39	135	>25
	425	525	8	4	1	0	0	0	0	0	2	48	260	>25
	425*	525	9	3	1	0	0	0	0	0	2	48	250	>25
	450	550	9	0	0	0	1	1	2	0	4	41	151	>25
K28-Mid.Cont. Kero.+	400	500	8	5	0	0	0	-	-	-	1	81	>300	0.17
Alkylate	400	500	9	4	0	0	0	-	-	-	1	76	>300	0.42
Before Storage	425	525	8	2	0	1	2	-	-	-	4	75	>300	0.49
	450	550	9	0	1	0	3	-	-	-	4	66	>300	1.98
After 26 wks. Sealed	400	500	7	2	2	1	1	0	0	0	4	57	>300	8.37
Storage at 110 F	400	500	8	0	3	1	1	0	0	0	4	50	298	>25
	425	525	6	1	1	0	2	1	2	0	6	42	167	>25
	450	550	5	0	1	1	1	0	2	3	7	40	141	>25
After 26 wks. Vented	400	500	8	2	1	2	0	0	0	0	3	60	>300	4.92
Storage at 110 F	400	500	9	1	2	1	0	0	0	0	3	48	258	>25
	425	525	6	1	1	0	2	3	0	0	5	43	173	>25
	450	550	6	2	0	0	1	1	3	0	6	42	166	>25
K29-Gulf Coast Kero.	400	500	10	0	3	0	0	-	-	-	2	54	>300	13.3
+ Alkylate	400	500	9	2	2	0	0	-	-	-	2	56	>300	9.97
Before Storage	425	525	9	0	0	1	3	-	-	-	4	47	240	>25
	450	550	7	0	0	1	5	-	-	-	4	44	195	>25
After 26 wks. Sealed	400	500	8	2	3	0	0	0	0	.0	2	49	273	>25
Storage at 110 F	400	500	7	1	3	0	2	0	0	0	4.	45	204	>25
	425	525	8	2	2	0	0	1	0	0	5	39	131	>25
	450	550	8	0	1	0	0	2	2	0	6	36	108	>25
After 26 wks. Vented	375	475	9	4	0	0	0	0	0	0	1	48	266	>25
Storage at 110 F	400	500	8	0	4	1	0	0	0	0	3	46	221	>25
	400	500	6	1	2	1	3	0	0	0	4	44	186	>25
	425	525	3	4	2	0	2	2	0	0	5	41	150	>25
	450	550	3	4	1	0	0	2	3	0	6	35	97	>25
K30-West Texas Kero.	400	500	8	3	2	0	0	-	-	-	2	57	>300	8.80
+ Alkylate	400	500	5	6	2	0	0	-	-	-	2	66	>300	1.85
Before Storage	425	525	7	0	1	2	3	-	-	-	4	51	>300	21.00
	450	550	7	0	1	1	4	-	-	-	4	49	270	>25
After 26 wks. Sealed	400	500	7	5	1	0	0	0	0	0	2	50	292	>25
Storage at 110 F	400	500	9	0	4	0	0	0	0	0	2	48	252	>25
	400*	500	7	5	1	0	0	0	0	0	2	62	>300	3.68
	425	525	8	2	2	1	0	0	0	0	3	54	>300	13.32
	450	550	7	2	1	1	2	0	0	0	4	54	>300	12.67
After 26 wks. Vented	400	500	11	2	0	0	0	0	0	0	1	59	>300	5.65
Storage at 110 F	400	500	9	2	2	0	0	0	0	0	2	48	266	>25

*After filtering through #2 Whatman and twice through 0.45 millipore paper.
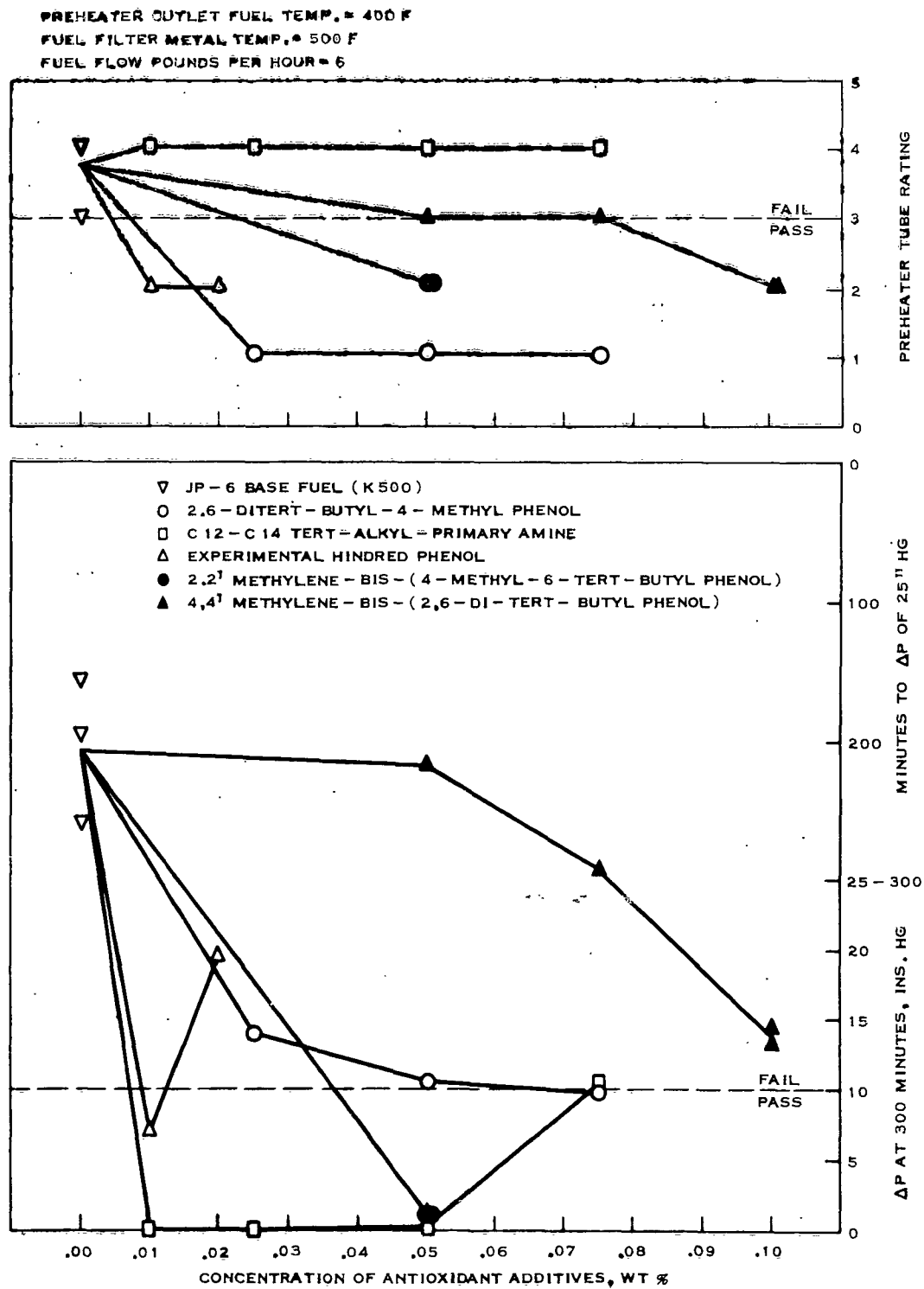
FIGURE 32
ASTM—CFR FUEL COKER DATA ON JP—6 JET FUEL BLENDS CONTAINING
ANTIOXIDANT FUEL ADDITIVES

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2" PIPE PACKED WITH
LINDE 4A MOLECULAR SIEVE

5 MICRON PUROLATOR FILTERS

HOT ROOM STORAGE DRUMS

AMBIENT STORAGE DRUMS

SUPPLY DRUMS
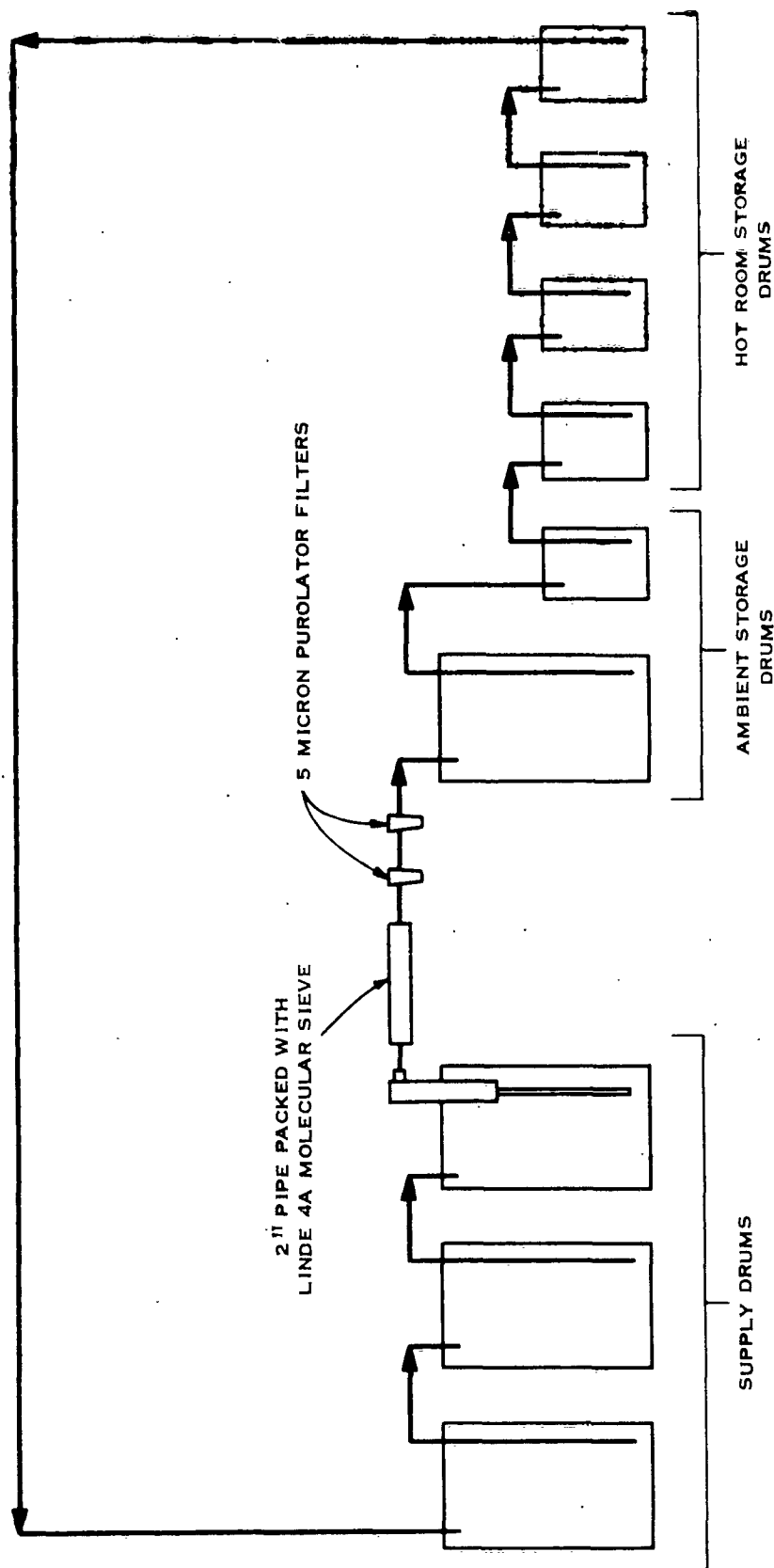
NOTE : MIXING TIME ABOUT 8 HOURS AT 1 GPM

FIGURE 33

SYSTEM FOR ACHIEVING UNIFORM LEVEL OF DRYNESS AND SOLIDS CONTAMINATION FOR
JP–6 STORAGE FUELS

62
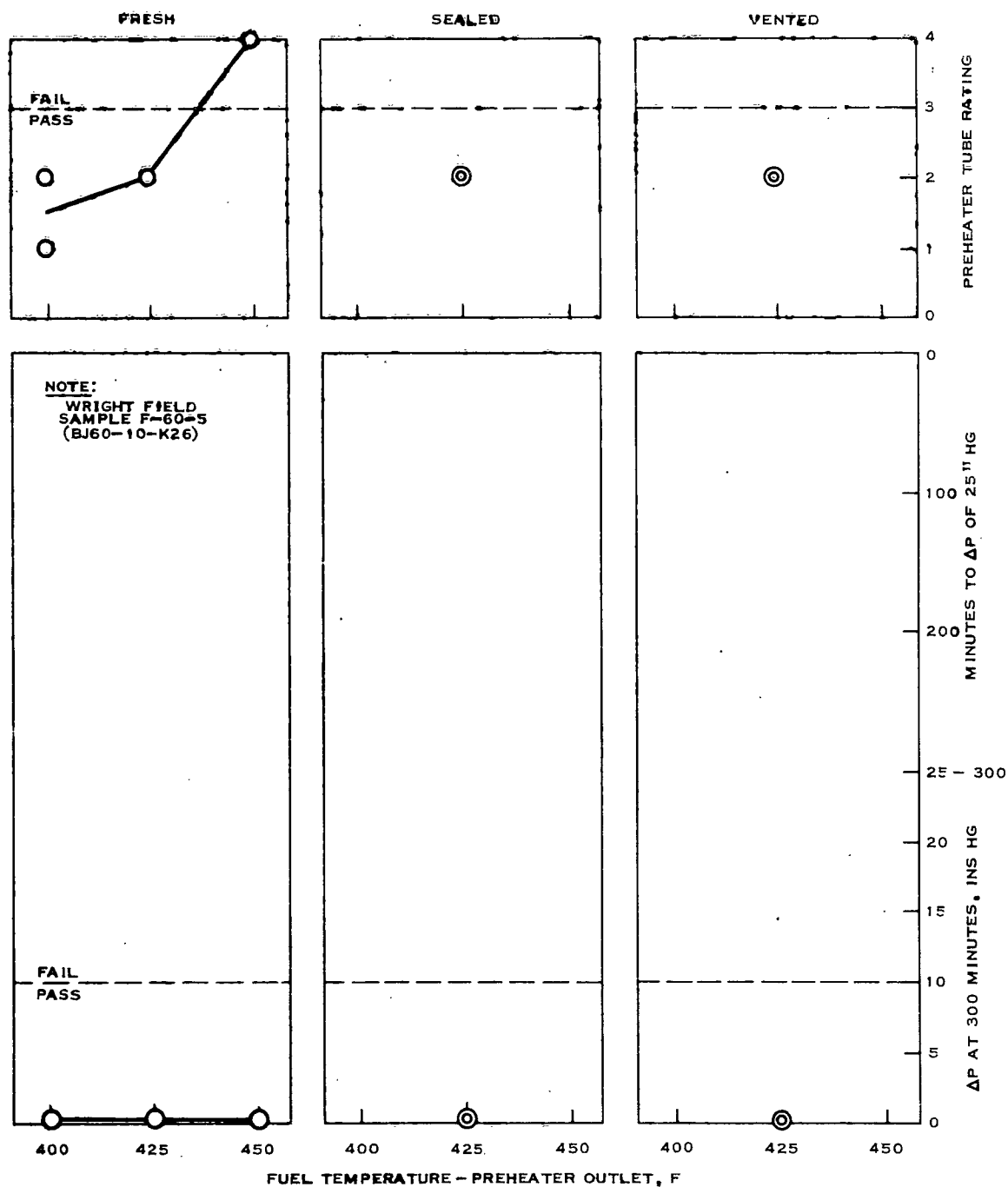
FIGURE 34
EFFECTS OF 26 WEEKS STORAGE AT 110 F ON CFR FUEL COKER RATINGS
AT VARIOUS TEMPERATURES FOR A JP-6 JET FUEL

63
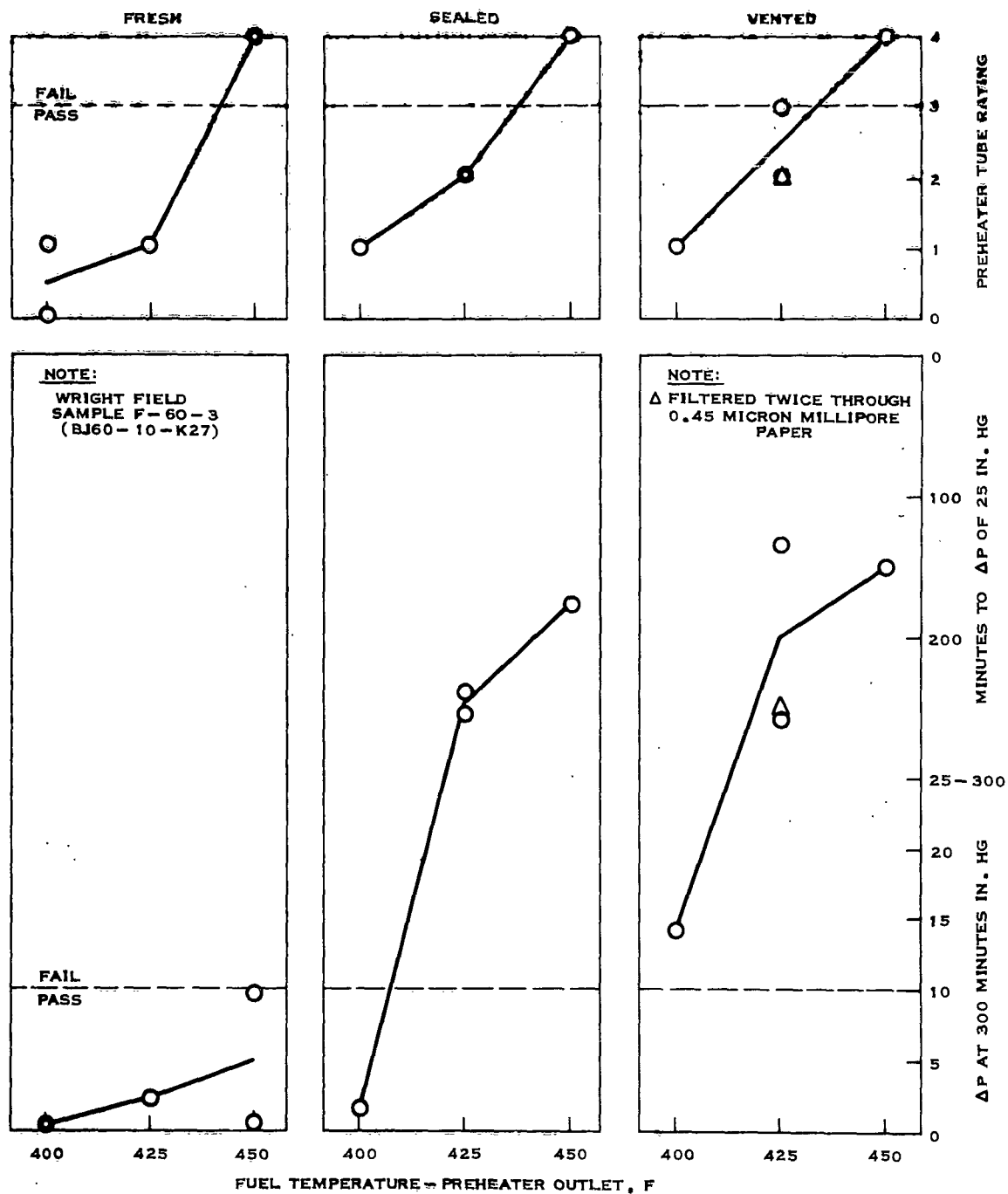
FIGURE 35
EFFECTS OF 26 WEEKS STORAGE AT 110 F ON CFR FUEL COKER RATINGS
AT VARIOUS TEMPERATURES FOR A JP–6 JET FUEL

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FIGURE 36
EFFECTS OF 26 WEEKS STORAGE AT 110F ON CFR FUEL COKER RATINGS
AT VARIOUS TEMPERATURES FOR A JP-6 JET FUEL
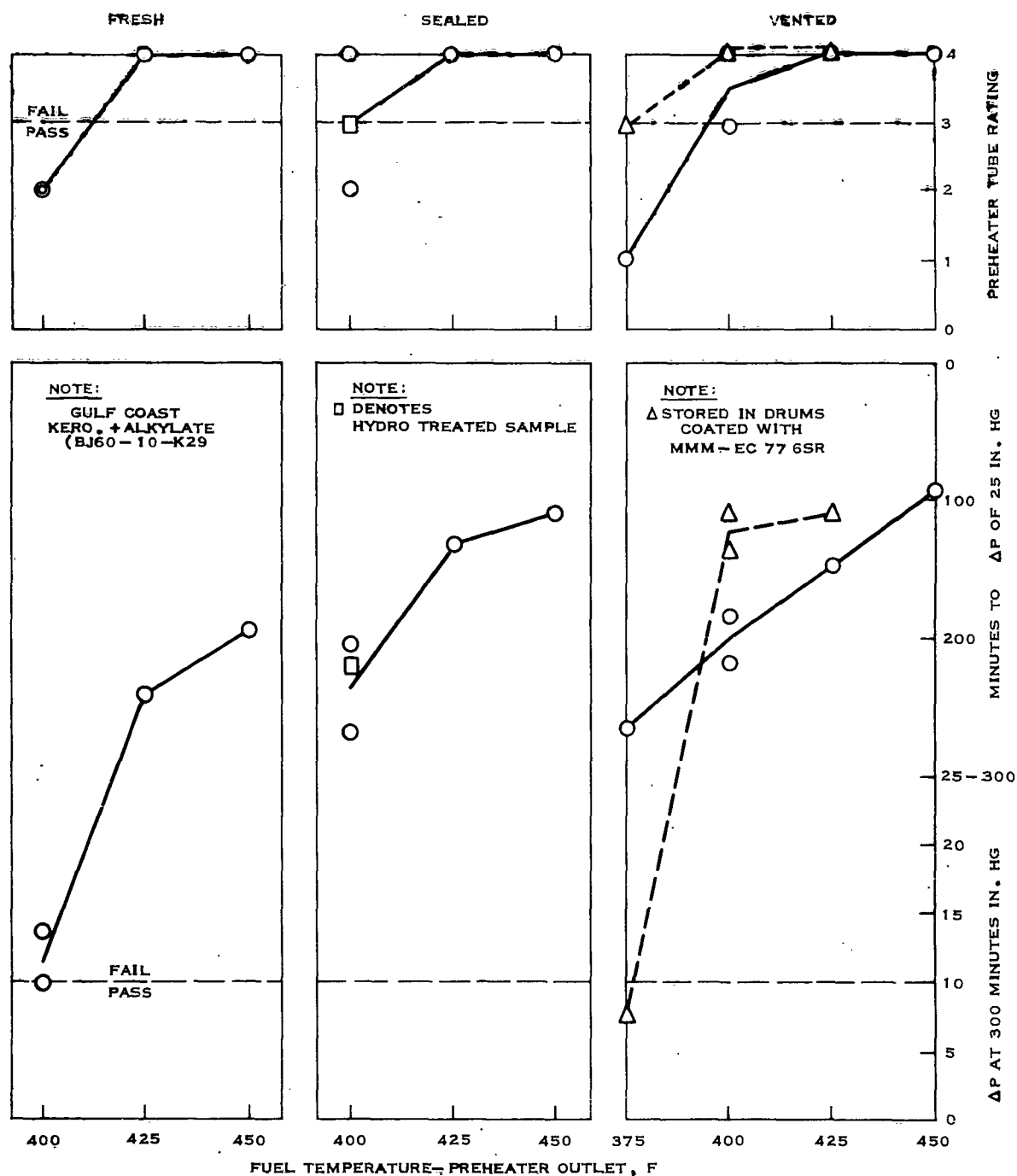
FIGURE 37
EFFECTS OF 26 WEEKS STORAGE AT 110 F ON CFR FUEL COKER RATINGS
AT VARIOUS TEMPERATURES FOR A JP-6 JET FUEL

66
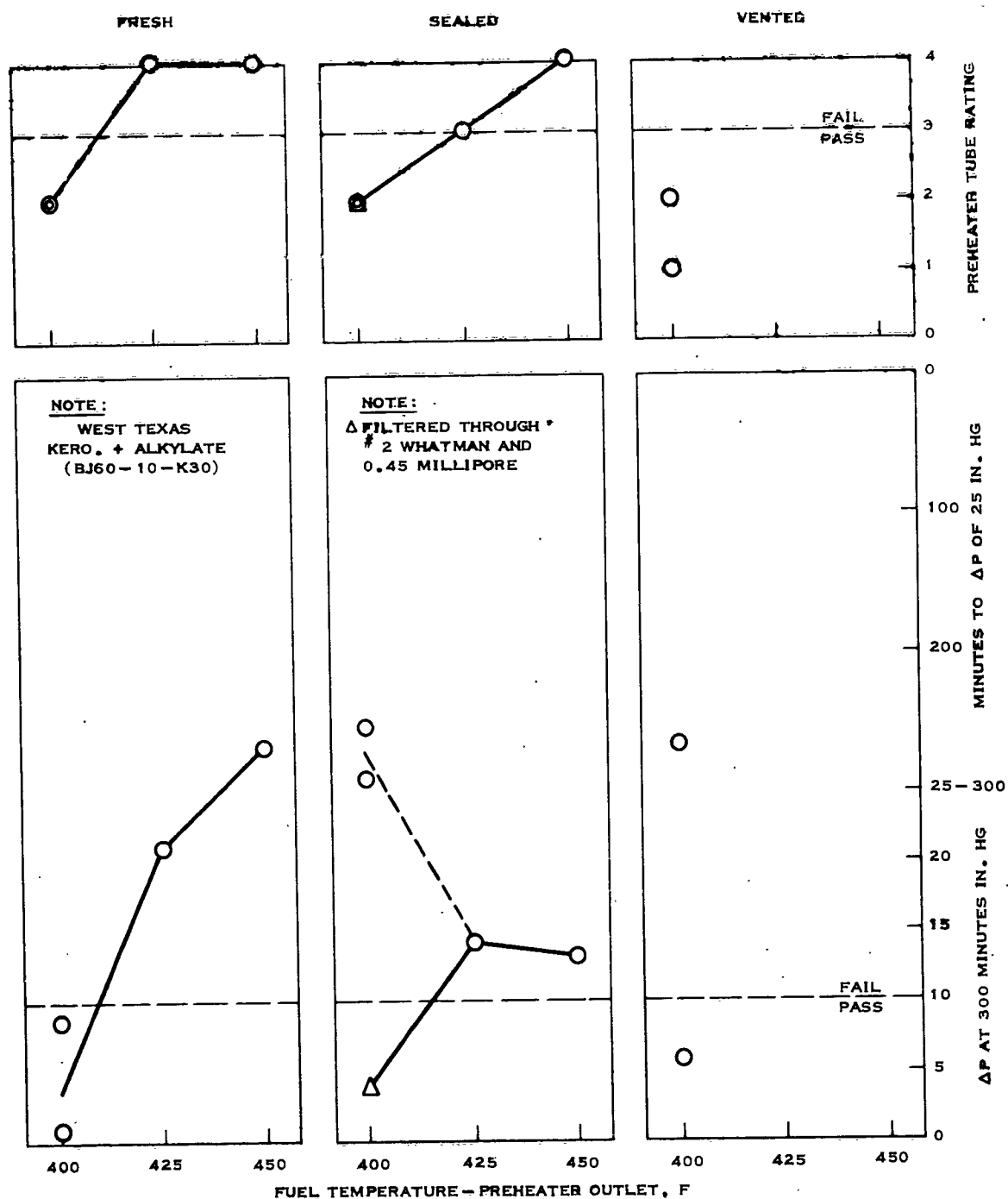
FIGURE 38
EFFECTS OF 26 WEEKS STORAGE AT 110 F ON CFR FUEL COKER RATINGS
AT VARIOUS TEMPERATURES FOR A JP-6 JET FUEL

have been removed by the normal prefiltration and thus have caused filter plugging in the Coker tests with the after-storage samples. Figure 34 shows that this was not the case, the test with 0.45 micron prefiltration agreeing closely with the two tests at 425-525 F using normal prefiltration. Thus the indicated deterioration in CFR Fuel Coker performance for this fuel is believed due to chemical alteration in composition, rather than contamination by solids.

Figure 36 shows that fuel K28, which ranked intermediate in thermal stability quality when fresh, deteriorated badly in this respect during storage in terms of both filter plugging and preheater rating. Hydrotreating one of the after-storage samples of this fuel under conditions effective for the removal of sulfur, basic nitrogen and naphthalene nucleus aromatic compounds did not restore the thermal stability rating of this fuel to the original (fresh condition) level.

Considering the two fuels which were borderline in quality when fresh, Figure 37 shows that fuel K29 also deteriorated significantly in CFR Fuel Coker rating during storage, in terms of both filter plugging and preheater deposit rating, and was helped no more by hydrotreating than was fuel K28. Storage of extra samples of this fuel in drums lined with MMM-EC776SR top coating also showed deterioration, but not believed significantly greater than observed in the uncoated containers. Fuel K30 however (Figure 38), also borderline in quality to start with, showed evidence of storage deterioration with only one of the storage drums and then only in terms of the filter plugging phase of the CFR Fuel Coker test. This effect was traced to a rise in solids contamination, by means of an extra test employing prefiltration through both 3.0 micron and 0.45 micron filter paper which produced a rating comparable to the fresh sample. Thus the second vented drum sample of this fuel was left in storage for an additional three months -- the overall thermal stability level of this sample in the absence of solids contamination not being significantly poorer than when fresh.

Note that the relative effects of vented versus sealed-under-nitrogen storage were nil - implying that, if the chemical mechanism causing the deterioration in thermal stability rating of fuels K27, 28, 29 is oxidative in nature, the small amounts of oxygen dissolved in the fuels to begin with more than suffice for the oxygen-consuming reactions leading to these effects.

The effects of storage on the antioxidant additive blends is shown by the CFR Fuel Coker ratings listed completely in Table VIII and in the form of bargraphs at 400-500 F temperature condition only in Figure 38. First of all the change in rating for the base fuel alone after 26 weeks at 110 F was not quite enough to allow saying with assurance that it had deteriorated -- preheater deposit ratings averaged about the same as when fresh while the filter plugging results were somewhat poorer. Therefore the second drum of this material was left in storage for an additional three month period. It might be mentioned that this fuel was not tested at temperatures above 400-500 F when fresh, since it was already "failing" in terms of the JP-6 specification at this level.

All of the additives were blended in this base fuel to concentrations at which at least a borderline "pass" was approached in the fresh state, though with the mixed C_{12}-C_{14} tertiary alkyl primary amines this was possible only in terms of filter plugging. As to storage effects, blend K35 with 0.10 wt.per cent 4,4' methylene bis(2,6-ditertiary butyl phenol) as the additive appeared unchanged

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TABLE XXII

THERMAL STABILITY OF A JP-4 BASE FUEL CONTAINING ANTIOXIDANT ADDITIVES

Fuel Ident: BJ60-10-	Test Temperature Preheater	Filter	Tube Ratings								Max. Rating	Filter Merit Rating	Minutes to 25" Hg ΔP	ΔP ins. Hg at 300 Minutes
			0	1	2	3	4	5	6	7				
K500-Base*	400	500	3	2	2	0	6	–	–	–	4	42	160	>25
Before Storage	400	500	8	3	.1	1	0	–	–	–	3	48	257	>25
	400	500	8	1	1	2	1	–	–	–	4	45	197	>25
After 26 wks. Vented	400	500	4	1	5	3	0	0	0	0	3	35	96	>25
Storage at 110 F	400	500	4	2	4	3	0	0	0	0	3	33	86	>25
K31-Base + 0.05 wt. % (1)	400	500	9	4	0	0	0	–	–	–	1	55	>300	10.60
Before Storage	400	500	7	3	3	0	0	–	–	–	2	47	240	>25
	450	550	7	0	3	0	3	–	–	–	4	45	202	>25
After 26 wks. Vented	400	500	3	5	5	0	0	0	0	0	2	47	245	>25
Storage at 110 F	400	500	4	5	3	1	0	0	0	0	3	47	241	>25
K32-Base + 0.01 wt. % (2)	400	500	1	3	4	1	4	0	0	0	4	99	>300	0.02
Before Storage	400	500	5	3	0	0	2	1	2	0	6	99	>300	0.01
After 26 wks. Vented	375	475	8	1	0	0	2	0	1	1	7	86	>300	0.08
Storage at 110 F	375	475	8	1	0	0	2	0	1	1	7	81	>300	0.18
	400	500	7	1	0	0	0	0	0	5	7	26	54	>25
	400	500	7	1	0	0	0	0	0	5	7	29	66	>25
K33-Base + 0.01 wt. % (3)	400	500	7	3	3	0	0	0	0	0	2	58	>300	7.04
Before Storage	400	500	4	1	3	2	3	0	0	0	4	56	>300	10.15
	450	550	3	2	.0	3	5	0	0	0	4	47	237	>25
After 26 wks. Vented	400	500	3	1	5	4	0	0	0	0	3	55	>300	10.10
Storage at 110 F	400	500	3	4	5	1	0	0	0	0	3	48	252	>25
K34-Base + 0.05 wt. % (4)	400	500	4	1	8	0	0	0	0	0	2	75	>300	0.47
Before Storage	400	500	3	2	8	0	0	0	0	0	2	77	>300	0.35
	450	550	2	2	2	5	2	0	0	0	4	38	122	>25
After 26 wks. Vented	375	475	0	5	5	3	0	0	0	0	3	72	>300	0.80
Storage at 110 F	400	500	0	3	5	3	2	0	0	0	4	55	>300	12.00
	400	500	3	1	5	4	0	0	0	0	3	47	245	>25
	425	525	1	0	6	3	3	0	0	0	4	36	101	>25
K35-Base + 0.10 wt.% (5)	400	500	4	8	1	0	0	0	0	0	2	53	>300	14.85
Before Storage	400	500	3	6	4	0	0	0	0	0	2	54	>300	12.88
	450	550	2	1	1	4	4	1	0	0	5	33	87	>25
After 26 wks. Vented	400	500	5	0	6	2	0	0	0	0	3	61	>300	2.17
Storage at 110 F	400	500	3	4	6	0	0	0	0	0	2	54	>300	12.32
K53-K29(6) Stored in drums	375	475	9	0	3	1	0	0	0	0	3	58	>300	7.40
coated inside with EC776SR	400	500	0	7	2	1	1	2	0	0	5	39	133	>25
for 26 wks. at 110 F	400	500	6	1	1	2	2	1	0	0	5	37	112	>25
	425	525	7	1	1	0	2	1	1	0	6	37	111	>25

*Composition: Gulf Coast Kerosine + Alkylate

(1) 2,6-di-tert-butyl-4-methyl phenol
(2) Mixed C_{12}-C_{14} tertiary alkyl primary amines.
(3) Experimental hindered phenol.
(4) 2-2, methylene-bis-4-methyl-6-tertiary butyl phenol)
(5) 4,4' methylene-bis-(2,6-di-tert-butyl phenol)
(6) Gulf Coast kerosine + alkylate

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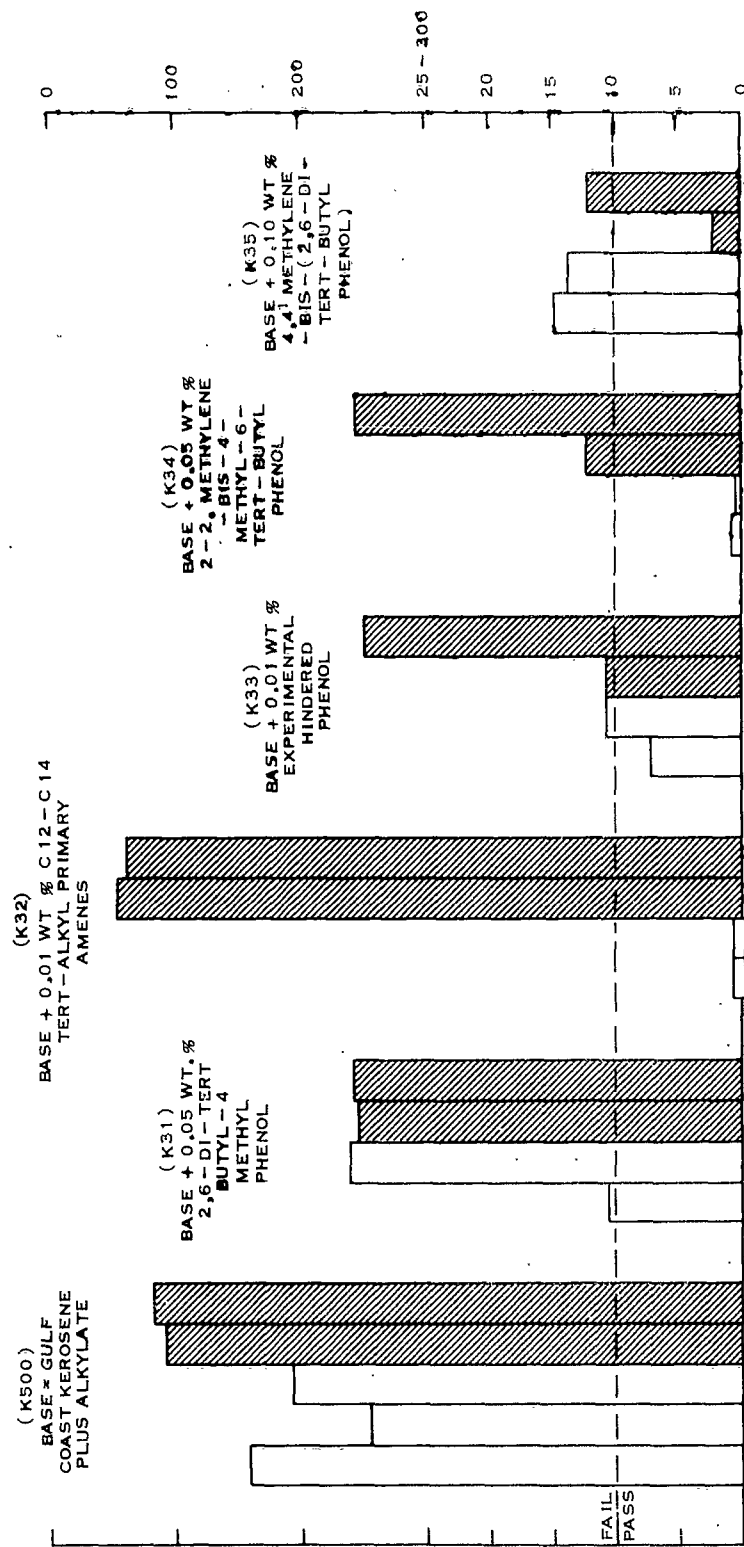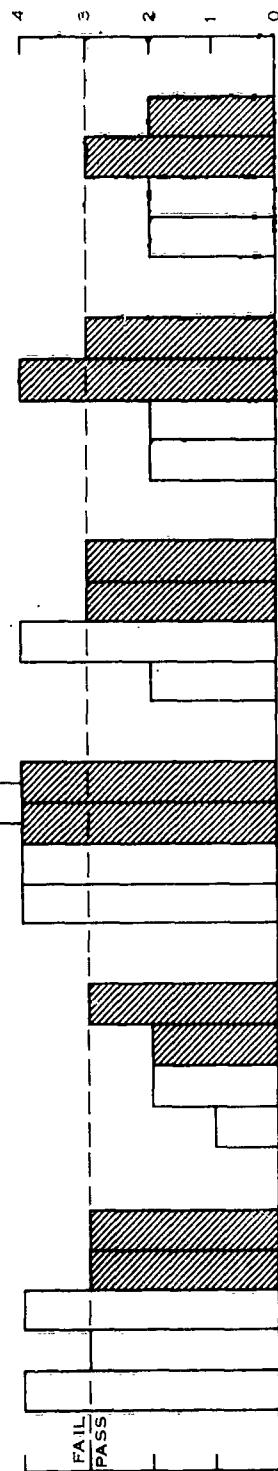
FIGURE 39

CFR FUEL COKER RATINGS OF A BASE FUEL CONTAINING ANTIOXIDANT ADDITIVES

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in thermal stability quality after 26 weeks at 110 F. Blend K31 with 0.05 weight
per cent 2,6-ditertiary butyl 4-methyl phenol showed some change in the negative
direction at this time but not enough to be considered conclusive, as was also the
case with blend K33 with 0.01 weight per cent of an experimental commercial hindered
phenol type additive. The second drum samples of these three additive blends were
therefore retained in storage for further comparison with the base fuel after an
additional three months time.

However, blend K32 with 0.01 weight per cent $C_{12}-C_{14}$ tertiary alkyl primary
amines showed by far the most striking negative change in performance after storage
of any test fuel in this program, in terms of both filter plugging and preheater -
deposit color rating -- apparently denoting oxidative deterioration of the additive
itself. Blend K34 with 0.05 weight per cent 2,2' methylene bis(4-methyl-6-tertiary
butyl phenol), the highest ranking of the blends when fresh, also showed definite
deterioration in this respect though still ranking superior to the base fuel after
storage. Therefore the second drum samples of the latter two blends were removed
from storage for CFR Fuel Coker testing at other temperature conditions, to reinforce
these indications of deterioration.

2. Chemical and Physical Properties

The results of the extensive chemical analyses and physical inspection test
work performed on the JP-6 storage samples are listed in Table IX for the non-addi-
tive-containing fuels both fresh and after 26 weeks storage at 110 F. First of
all, it is shown that these fuels all are very low in non-hydrocarbon constituents
such as sulfur and nitrogen compounds, suggesting that the reduction of such
impurities to very low levels is a byproduct of the JP-6 specification requirement
for 400 F-plus thermal stability performance. Considering two specific types of
sulfur and nitrogen compounds which have often been associated with temperature
instability effects in past work with other types of jet fuel, pyrrole nitrogen
level was found to be less than 0.4 ppm in all five test fuels while thiophenol
sulfur was less than 0.001 weight per cent as indicated by mercaptan sulfur analyses
(part-per-million level mercaptan analyses are in progress).

In all but one of these fuels existent and potential gum ratings were
essentially nil, while with the fifth (K26) fuel, indications of borderline gum
values were traced to the presence of a heavy oily contaminant soluble in normal
heptane and apparently harmless from the thermal stability standpoint. In no
case were the effects of storage manifested by a rise in gum content matching the
changes in CFR Fuel Coker rating discussed earlier.

As to the effects of the CFR Fuel Coker test itself at any given time period,
the most pronounced and consistent were sharp rises in peroxide level. In the
only two cases where this was not indicated, the fresh samples of fuels K29 and
30, there was a delay of several weeks between the submission of the after-Coker-
test samples and performance of the analysis which may have allowed some of the
peroxides to react further to more stable types of hydrocarbon oxidation products.
These data at any rate confirm that oxidation does take place under the inviron-
mental conditions provided by the CFR Fuel Coker at 400 F-plus temperature
conditions. Peroxide level showed no large nor consistent changes during storage
with any of the test fuels however, nor could infrared spectra run on the
complete fuels before and after storage (using the icebox "pseudo-fresh" samples)

TABLE IX

PHYSICAL AND CHEMICAL ANALYSIS DATA ON JP-6 STORAGE FUELS

B/60-10-

		K 26 26 Wks. 110 F Storage			K 27 26 Wks. 110 F Storage			K 28 26 Wks. 110 F Storage			K 29 26 Wks. 110 F Storage			K 30 26 Wks. 110 F Storage			K 500 26 Wks. 110 F Storage	
		Fresh	Sealed	Vented	Fresh	Sealed	Vented	Fresh	Sealed	Vented	Fresh	Sealed	Vented	Fresh	Sealed	Vented	Fresh	Sealed	Vented
Distillation: D86	IBP	314	310	316	302	301	304	313	318	322	309	314	314	320	320	319	320	318
	5%	334	332	331	319	314	317	337	332	335	330	328	328	334	347	328	332	330
	10%	337	335	334	324	319	321	346	342	342	335	337	337	337	334	333	336	335
	50%	348	346	346	346	345	345	385	384	384	378	378	379	369	363	364	366	364
	90%	368	366	365	408	407	407	454	452	452	451	452	450	462	456	456	458	456
	95%	376	373	372	439	442	442	468	467	467	462	462	462	488	482	482	485	482
	EP	438	407	407	497	480	480	506	482	483	480	476	476	516	510	512	516	514
	Recy.	99	99	99	99	99	99	99	99	99	99	99	99	99	99	99	99	99
	Res.	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
API Gravity @ 60 F		43.9	44.0	43.8	48.3	48.5	48.4	48.4	48.3	48.3	49.1	49.1	49.1	50.1	50.4	50.4	50.4	50.4
Steam Jet Gum, 450 F mg/100 ml		8.5(a)	7.6	8.7	0.02	0.00	0.00	0.00	0.3	0.8	0.00	0.00	0.4	0.00	0.5	0.3	0.5	0.3
16 Hr. Steam Jet Gum, 450 F mg/100 ml		9.2			0.02			0.0			0.00			0.8			0.6	
Lamp Sulfur: Before Test Wt. %		<0.001	0.001	0.001	0.010	0.011	0.013	0.017	0.018	0.018	0.005	0.007	0.007	0.003	0.003	0.005		0.003
After Test Wt. %		<0.001			0.010	0.011	0.011	0.017	0.017	0.017	<0.02(x)	0.007	0.007	0.01(x)	0.003	0.003		0.003
Mercaptan Sulfur: Before Test Wt. %		<0.001			<0.001			<0.001			<0.001			<0.001				
After Test Wt. %		<0.001			<0.001			<0.001			<0.001			<0.001				
Freezing Point, °F		<-100			-85			-58			-57			-60				
Net Btu/lb.		18680			18632			18681			18710			18745				
Viscosity at -40 F cs		5.54			5.08			8.87			8.82			8.21				
100 F cs		1.162			1.092			1.355			1.354			1.308				
210 F cs		0.620			0.592			0.693			0.697			0.695				
Aromatics FIA Vol. %		2.2	1		14.3	1		9.2	1		7.8	1		8.7	1	1b		1
Olefins Vol. %		1.0	1	1b	<1.0	1		<1.0	3	2	2.6	1b		2.3	1b			1
Smoke Point mm		29.8			26.8			27.7			29.7			29.7				
Luminometer Number		67.0			52.2			62.9			63.7			68.2				
Corrosion		1b	1	1b	1b	1	1	1	1	1	1	1b	1b	1b	1b	1b		1b
Water Reaction		<80	1		100	1	2	1b	3	2	1b	1	1	116	1			1
Flash Point		135.2			136.8			154.6			114			159.1				
Aniline Point		5935			6607			7405			158.7			7971				
Aniline-Gravity Product											7792							
Water Content ppm		30	25	11	40	21	26	32	33	6	45	68	<5	28	29	37		
Particulate Matter mg/l		-	-	-	0.3	90.9(e)	97.4(e)	0.6	2.0(b)	2.6(c)	0.8	0.9	2.3	0.4	2.6	1.5		
Saybolt Color: Fresh		+30	+26	+22	+17	+13	+13	+20	Yellow	Yellow	+30	+4	+6	+24	+22	+20	+30	+28
After filtering		+30	+18	-	+18	+13	+13	+19	Yellow	Yellow	+26	-5	+4	+24	+21	+9	+30	+20
After Test		-	-	+18	-	-2	-2	-	Yellow	Yellow	-	+13	+13	+19	+19	+18	-	+19
Neutralization Number		0.00	0.20	0.22	0.04	0.03	0.02	0.04	0.04	0.02	0.04	0.02	0.01	0.04	0.00	0.02		0.05
Total Nitrogen: Before Test ppm		6.0			9.3			3.5			7.0			4.5				
After Test ppm		7.3			5.2			3.9			4.6			3.6				
Pyrrole Nitrogen: Before Test ppm		<0.1	<0.1	<0.1	0.3	0.2	0.2	0.3	0.4	0.4	0.2	0.2	0.2	0.2	0.2	0.3		0.2
After Test ppm		<0.1	<0.1		0.2	0.2	0.2		0.4	0.3		0.2	0.2		0.2	0.2		0.2
Basic Nitrogen: Before Test ppm		4.8	3.6	3.1	4.0	3.6	2.9	<1.0	1.69	0.99	1.0	1.70	1.61	1.5	0.87	0.87	0.9	9.2
After Test ppm		3.0	2.8	2.7	2.0	3.06	3.02	1.0	1.16	0.62	1.5	1.44	1.44	0.6	0.95	0.95	0.7	1.1
Polycyclic Aromatics: Before Test Wt. %		<0.01	0.011	0.010	0.9	0.91	0.94	1.7	1.81	1.81	2.9	2.78	2.78	1.0	0.96	0.98	0.9	0.95
After Test Wt. %		<0.01	0.0009	0.0009	0.9	0.95	0.96	1.7	1.81	1.81	2.8	2.80	2.84	0.9	0.96	0.98	1.0	0.97
Peroxides: Before Test ppm		0.5	<0.1	0.1	1.1	0.5	0.2	1.6	1.3	1.8	1.9	1.2	1.2	7.7	4.1	10.1		6.4
After Test ppm		9.6	10.5	20.0	15.1	7.4	9.4	9.4	5.8	6.6	1.1	10.7	14.7	4.5	9.8	12.2		7.3
Oxygen: Before Test Wt. %		0.02#	0.035	0.03	0.095	0.024	0.022	0.073	0.051	0.036	0.10	0.020	0.02	0.053	0.032	0.014		0.075
(Chromatographic): After Test Wt. %		0.05	0.021	0.04	0.09	0.016	0.025	0.076	0.025	0.035	0.039	0.025	0.025	0.038	0.085	0.06		
Bromine No.: Before Test		0.03	<0.05	<0.05	0.33	0.48	0.45	0.82	0.86	0.92	0.27	0.28	0.28	0.58	0.56	0.60		0.61
After Test		0.02	<0.05	<0.05	0.43	0.46	0.28	0.58	0.81	0.83	0.28	0.21	0.30	0.59	0.62	0.59		0.56
Soluble Copper (f) ppm		<0.1	<0.1	<0.1	0.14	0.2	0.2	<0.1	(d)	(d)	<0.1	0.1	0.1	<0.1	<0.1	<0.1	0.060	
Trace Copper (z) ppm		0.011	0.008	0.015	0.084	0.127	0.053	0.037	0.024	0.023	0.010		0.021	0.041	0.005	0.5##	<1.0	8.046
Soluble Iron ppm		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	0.010	
Soluble Lead ppm		-	-	-	<0.005	-		<0.005			<0.005			<0.005				
Chromatograms		No Change	No Change		No Change	No Change		No Change			No Change			No Change				
Infrared Spectra		No Change	No Change		No Change	No Change		No Change			No Change			No Change				
Thermal Stability (CFR Coker)		Good	Good	Good	Good	Fair	Fair	Good	Poor	Poor	Fair	Poor	Poor	Fair	Fair	Fair	Poor	Poor
Description		WADD Sample (F-60-5)			WADD Sample (F-60-3)			Mid Continent Kerosine plus Alkylate			Gulf Coast Kerosine plus Alkylate			West Texas Kerosine Plus Alkylate				

(a) 0.5 After heptane wash
(x) X-Ray Method
(b) 1.0 After ash
(c) 1.3 After ash
(d) Color interfered with Method
(e) Appears to be Linde 4A Molecular Sieve carried over from preparation of samples for storage.
(f) Neocuproine-Spectrophotometric Method
(g) Di-Ethyl Di-thio carbamate Extraction Method

detect the appearance of more stable types of hydrocarbon oxidation products.

Lamp sulfur values did not indicate depletion of this type of fuel impurity during the Coker test, either with the fresh or the aged fuels. However it may be significant that the three fuels which did deteriorate in thermal stability quality during storage were measurably higher in sulfur content than the other two -- even though all were far below permissible specification limits (<0.4 Wt. %) More precise analyses for sulfur are planned, using a method sensitive to part-per-million level concentrations.

The small changes in basic nitrogen analysis before and after Coker-testing are not now believed significant, nor do the differences in content of either basic or total nitrogen when fresh appear to fit any consistent pattern with respect to the storage performance of the different fuels.

Analyses for polycyclic aromatics by UV light absorption showed measurable concentrations of such materials in all but fuel K26, which was also the most thermally stable of the group both before and after storage. An earlier section of this report has shown (see Figure 6) the very marked difference in thermal stability performance between three different cuts fractionated from a marginal quality JP-6 blend (a reblend of the West Texas kerosine plus alkylate test fuel - K30). These tests, employing the thermal insulating effects of deposits laid down as a criterion, indicated the most thermally unstable constituents of this fuel to be concentrated in the 400 F-plus boiling fraction. Efforts were made to isolate by comparative gas chromatograms the materials which were depleted from this fraction in forming the deposits, passing samples before and after the thermal stability test through an F. & M. temperature-programmed gas chromatography apparatus employing silicone grease as a fixed phase. Results were somewhat inconclusive, but did indicate that whatever differences there were in these 400 F-plus boiling range before-and-after-heating samples were concentrated in the heavy ends. Samples of these heavy components were therefore "trapped" as they emerged from the gas chromatography apparatus and examined by infrared and ultraviolet spectroscopy. Naphthalene-nucleus aromatic hydrocarbons were identified in the trapped samples, suggesting that these or oxidized derivatives may be contributing to thermal instability at temperatures of 400 F and above.

Comparative gas chromatograms using the same equipment were also run on the fresh fuels before and after Coker testing and on the fresh versus the aged fuels. No changes in individual peaks could be detected reflecting either the hydrocarbon components in the fuel which had reacted to make the deposits laid down in the Coker or those which had reacted in the storage containers to produce the observed changes in performance. It has been concluded that for further application of gas chromatography to this analysis problem some auxiliary means of concentrating the deposit precursors, such as fractional distillation or selective adsorption, must be employed.

The Millipore particulate contamination tests showed small rises in level of filterable solids for fuels K28, K29 (vented) and K30 (sealed). With the latter fuel, it may be recalled that filterable solids in the <3.0 micron range did affect CFR Fuel Coker rating, as established by a separate test using a 0.45 micron prefiltration step in place of the standard 3.0 micron prefilteration

with Whatman #2 filter paper. The indications of very large increases in particulate contamination for both the sealed and vented samples of fuel K27 were traced to Linde 4A molecular sieve fines which must have been carried over from the preparation of the fresh sample. This material appears to be completely removed by the standard prefiltration procedure, since an extra Coker test using 0.45 micron prefiltration showed no difference in results.

Analyses for trace amounts of soluble iron showed all of the samples less than 1.0 ppm in this respect both before and after storage. Analyses for soluble copper were run initially on all the fuels using a technique accurate to 0.1 ppm. Following storage, it became apparent that fuel K28 had darkened in color sufficiently to prevent the use of this colorimetric analysis technique. In addition, it was desired to establish whether the slight indications of higher soluble copper levels for fuel K27 were significant – therefore the soluble copper analyses were repeated using a method accurate to 10 ppb. These results do show some spread in this respect, with fuel K27 the highest of the group by a factor of 2 or 3. Since this fuel did deteriorate in thermal stability rating during storage these results may be significant, considering that copper is a well-known pro-oxidation catalyst.

Soluble lead analyses were also made, to check the possibility of contamination by leaded gasoline with any of the fuels and its possible relationship to either long or short term temperature stability effects. In only one case was this measurable, with the additive base fuel K500. Since this fuel was blended identically to fuel K30 and yet performed significantly poorer in the CFR Fuel Coker test, the presence of lead may be significant and this possibility is to be checked with synthetic blends containing small amounts of tetraethyllead.

The total oxygen analyses serve mainly to show that oxygen level in the fuels themselves did not differ appreciably between the vented versus nitrogen-purged-and-sealed storage containers, which agrees with the lack of difference in thermal stability rating. If oxidation reactions were responsible for the changes in thermal stability after storage, apparently the small amounts of residual oxygen dissolved in the fuels themselves was more than enough. A better procedure for eliminating oxygen access to jet fuels would be to collect the fuels under nitrogen directly from the refinery fractionation facilities and to maintain it under this nitrogen atmosphere from this point on until it enters the combustion sections of the aircraft engines themselves.

Considering next the Saybolt color ratings for the group of fuels, it is apparent that the three fuels (K27, 28, 29) which deteriorated measurably in thermal stability after storage also darkened measurably in color -- fuel K28 falling off the limits of the Saybolt scale after storage. This suggests that formation of color bodies or chromophores, through selective oxidation of fuel constituents of relatively dense molecular structures, is associated with the thermal stability effects. This indication has accordingly been followed up by more detailed examination of the optical characteristics of these fuels using the Bausch and Lomb Spectronic 20 spectrophotometer employed for the 5 ml thermal stability bomb test discussed earlier.

In Figures 40 through 45 are plotted the detailed wavelength versus light transmission curves for the fuels described in Table IX. These were run on the
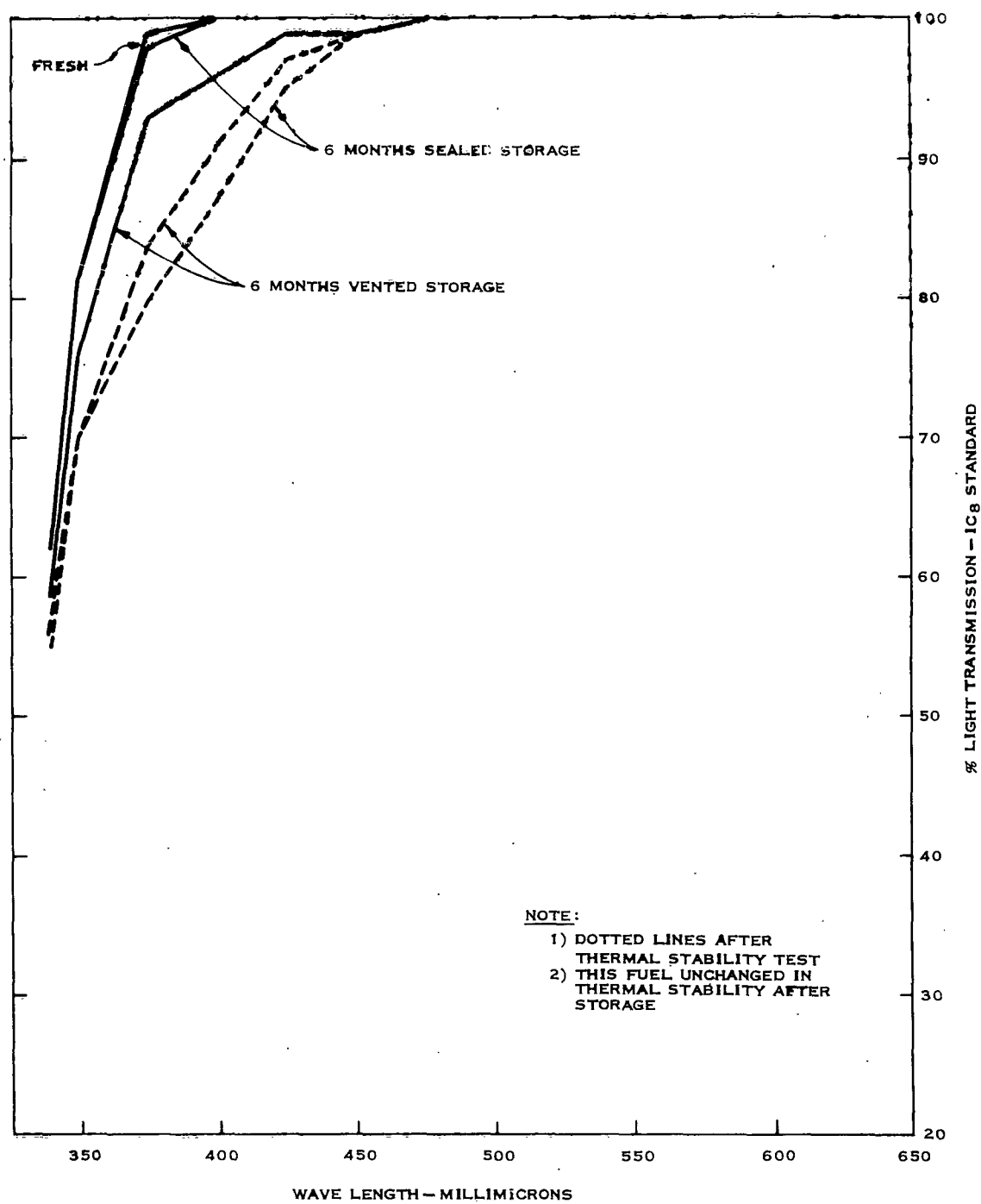
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FIGURE 40
LIGHT TRANSMISSION THROUGH JP−6 JET FUELS

FIGURE 41
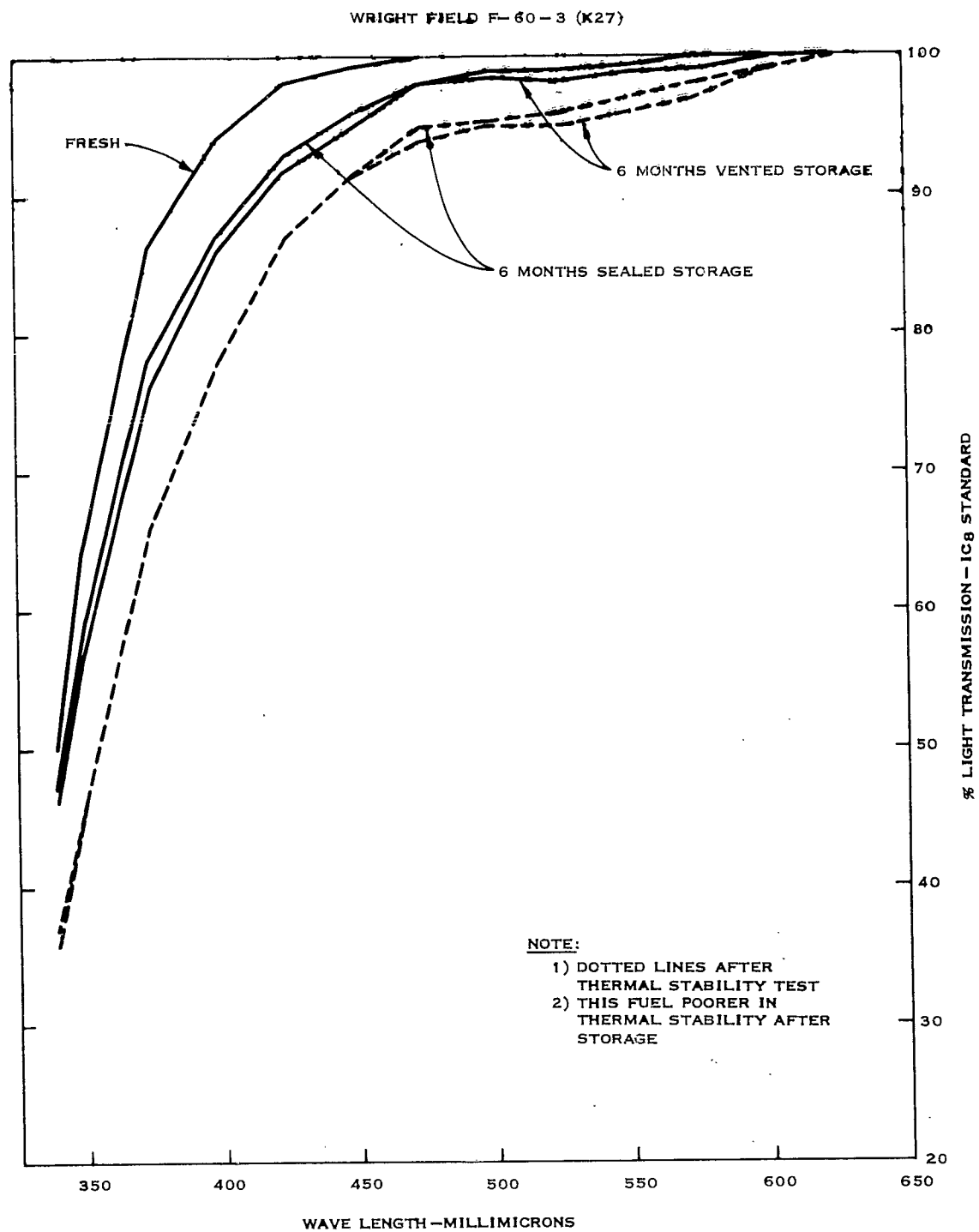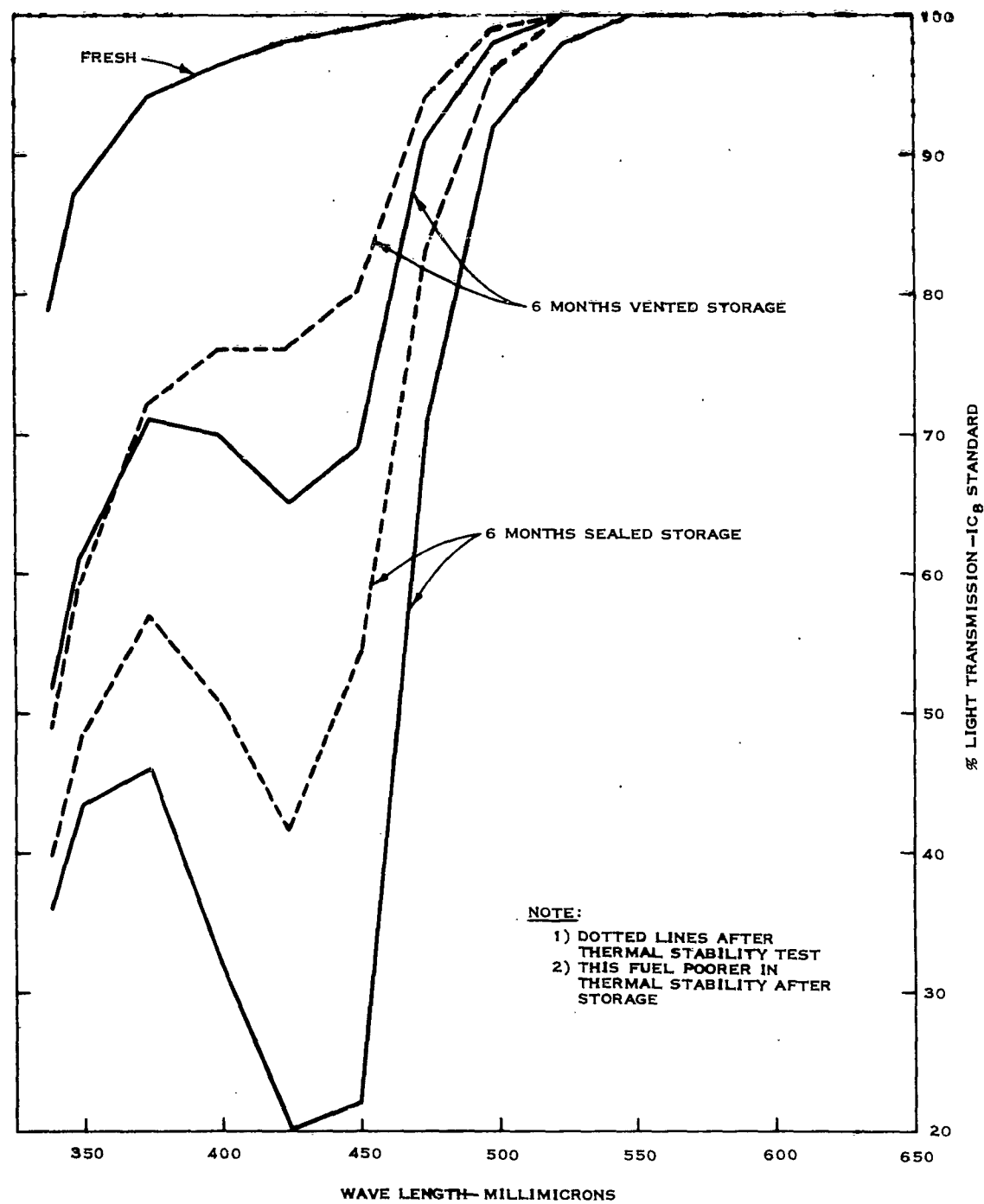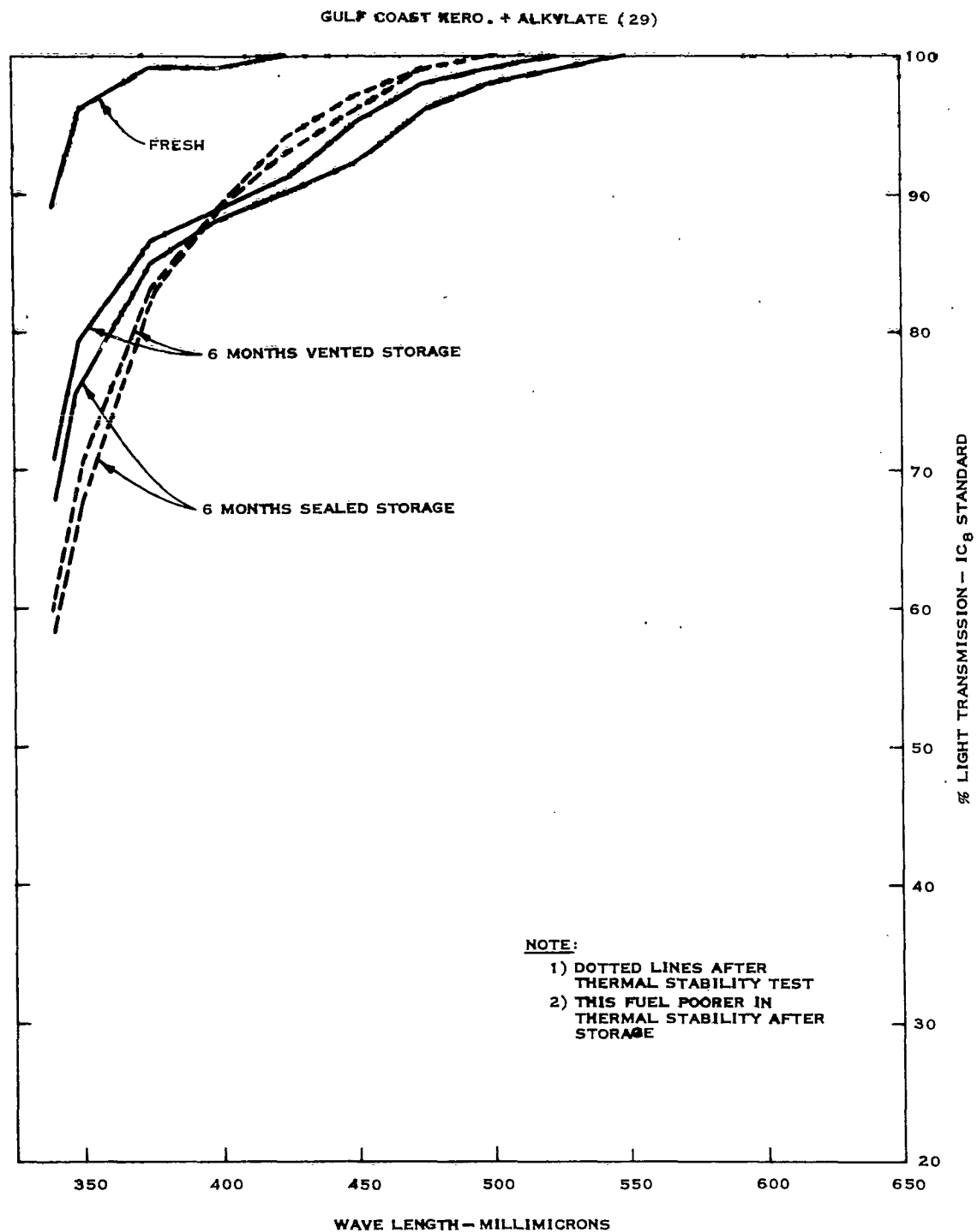LIGHT TRANSMISSION THROUGH JP—6 JET FUELS

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FIGURE 42
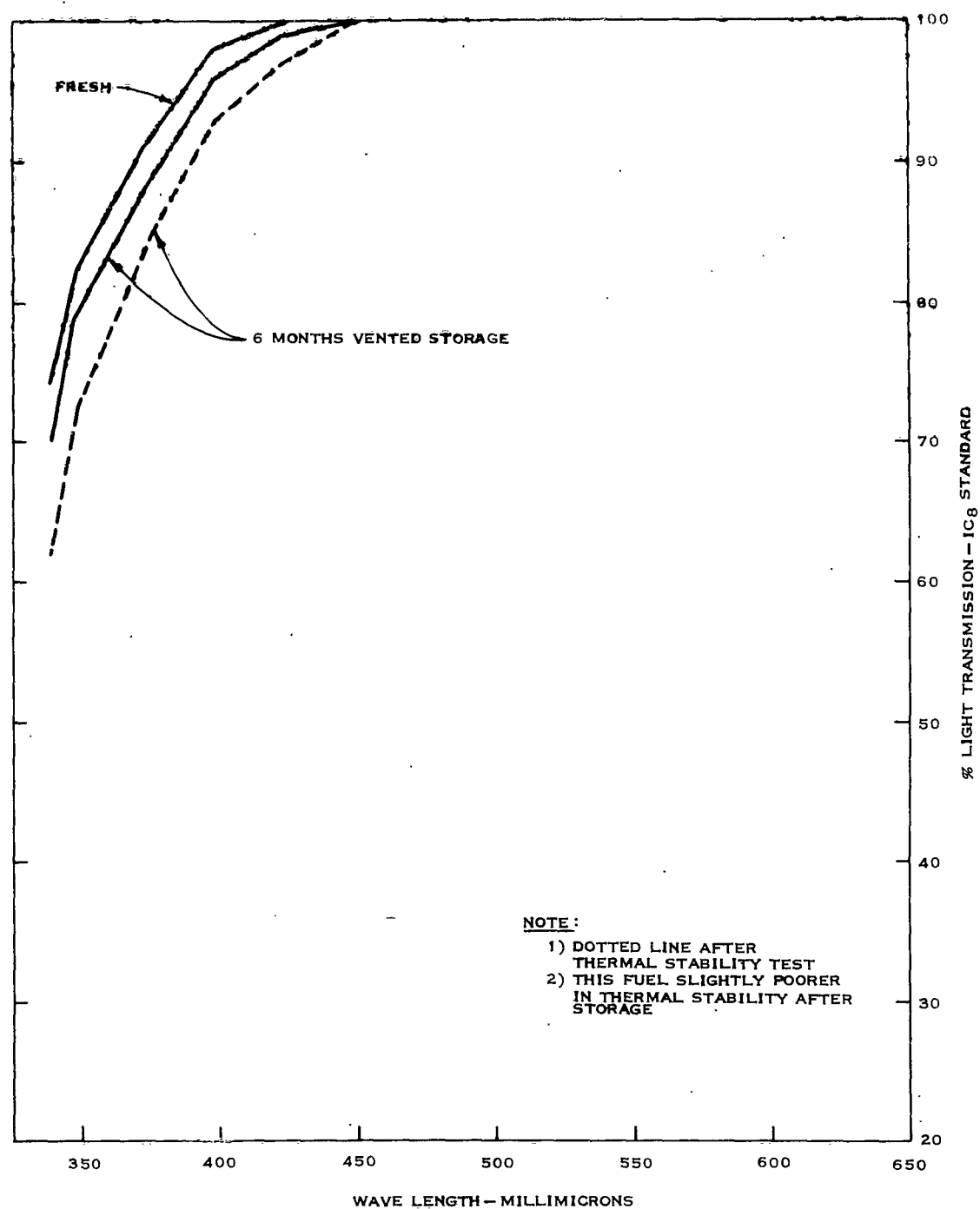LIGHT TRANSMISSION THROUGH JP−6 JET FUELS

GULF COAST KERO. + ALKYLATE (29)

NOTE:
1) DOTTED LINES AFTER THERMAL STABILITY TEST
2) THIS FUEL POORER IN THERMAL STABILITY AFTER STORAGE

FRESH

6 MONTHS VENTED STORAGE

6 MONTHS SEALED STORAGE

% LIGHT TRANSMISSION — IC$_8$ STANDARD

WAVE LENGTH — MILLIMICRONS

FIGURE 43
LIGHT TRANSMISSION THROUGH JP-6 JET FUELS

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WEST TEXAS KERO. + ALKYLATE (K30)
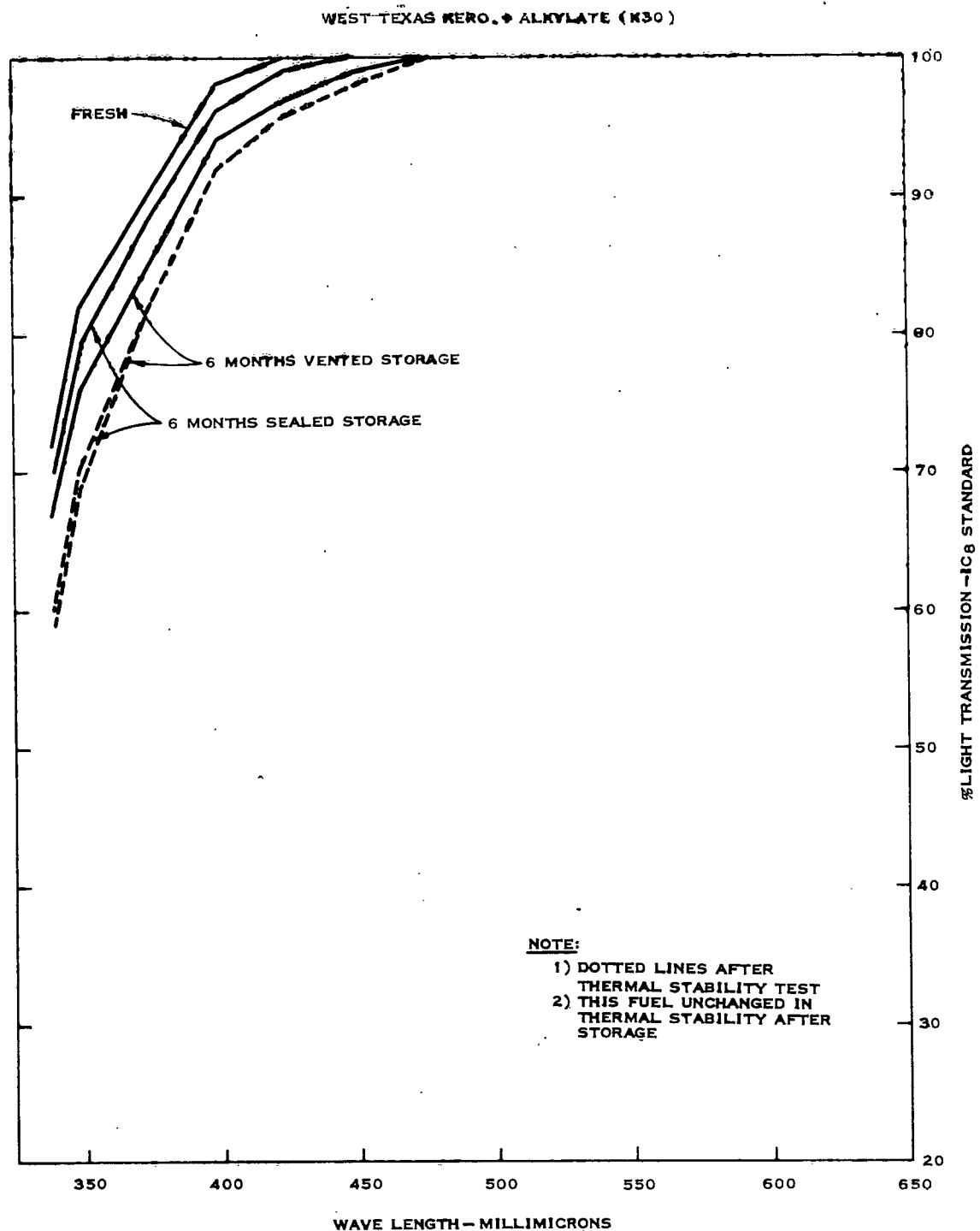
FIGURE 44
LIGHT TRANSMISSION THROUGH JP-6 JET FUELS

WEST TEXAS KERO. + ALKYLATE (K500)

FIGURE 45
LIGHT TRANSMISSION THROUGH JP-6 JET FUELS

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fuels both before and after CFR Fuel Coker testing at 400 F-plus temperatures. Note that for fuels K26, K30 and K500, which did not change significantly in thermal stability after storage, the change in light transmission over the 340-450 millimicron wavelength range was also very small. For the other three fuels significant losses in light transmission appeared to accompany the observed poorer performance in the CFR Coker test after storage, particularly fuel K28. This confirmed the trend shown by the Saybolt color ratings listed in Table IX. Light transmission decreased after heating during the CFR Coker test for all the fuels except K28, where the trend in the opposite direction perhaps indicates concentration of the color bodies in to the deposits left in the apparatus. This effect forms the basis for the 5 ml bomb thermal stability test described earlier.

Table X shows chemical and physical data obtained on the hydrotreated samples of Fuels K28 and 29, which it may be recalled failed to restore the thermal stability performance of these two fuels to the initial level prior to storage. Hydrotreating under these conditions reduced total sulfur levels in both fuels, reduced basic nitrogen and improved the Saybolt color ratings. It also dropped the polycyclic aromatic content significantly, the catalyst used having been selected for its ability to accomplish this -- however it is not known whether the reduction of naphthalenes represented complete hydrogen saturation of both rings or partial conversion to tetralin type structures. The fluorescent indicator absorption analyses show increased olefin level after hydrotreating, however this is not believed correct since the FIA technique is not considered meaningful by this laboratory for olefin concentrations below 5 per cent. Olefins calculated from bromine number show the expected reduction with hydrogen treatment. If the latter are accepted and the FIA aromatics values are corrected upwards correspondingly, then the comparison between total aromatics before and after hydrotreating show only slight changes. This would imply that perhaps the naphthalene nucleus compounds were only partially converted, to tetralin structures.

Following up the Saybolt color data in Table X, Figures 46 and 47 show complete wavelength versus light transmission curves for fuels K28 and 29 before and after hydrotreatment. Note that, although light transmission from 400 millimicrons on out through the visible range was greatly improved by hydrotreating, wavelengths below this level still showed much more absorption than the fresh fuels. Thus, compounds formed during storage of a nature such as to absorb ultraviolet light in the 350 millimicrons wavelength range appear related to thermal stability performance as defined by the CFR Fuel Coker.

This further supports the selection of the 350 millimicron wavelength band for use in the 5 ml thermal stability bomb test described earlier.

Table XI lists physical and chemical analysis results obtained on the blends of fuel K500 with antioxidant additives, and on fuel K29 after storage in drums lined with MMM-EC776SR. These data were accumulated both to aid interpretation of the thermal stability test work and to indicate whether the additives had undesirable side effects on fuel properties. No adverse effects on corrosion or water reaction characteristics were observed either before or after storage. The slightly higher potential gum rating for blend K33 was not borne out by an increase in existent gum after storage. However blend K32 (which became much worse in thermal stability rating following storage) also showed a large increase in existent

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TABLE X

EFFECT OF HYDROTREATING ON TWO JP-6 FUELS AFTER STORAGE

Fuel Ident:* BJ60-10-		K28A	K28AH	K29A	K29AH
Dist: D-86	IBP	318	310	314	306
	10%	342	339	337	333
	50	384	380	378	377
	90	452	452	452	446
	EP	482	488	476	480
	Recy.	99	99	99	99
	Res.	1	1	1	1
Lamp Sulfur,	Wt. %	.018	.003	.007	.002
Aromatics,	Vol. % } FIA	9.2	6.5	7.8	5.5
Olefins,	Vol. % }	<1.0	3.0	2.6	3.5
Olefins, Vol. % (Bromine No.)		0.85	0.12	0.27	0.10
Total Nitrogen,	ppm	3.5	4.2	7.0	3.9
Basic Nitrogen,	ppm	1.69	.33	1.70	.27
Polycyclic Aromatics,	Wt. %	1.81	.25	2.80	.28
Smoke Point,	mm	27.7	31.9	29.7	33.7
Saybolt Color		Yellow	+23	+4	+30
API Gravity		48.3	49.3	49.1	50.1
CFR Fuel Coker Data**					
Tube Rating		4	2	2	3
		4		4	
Filter Merit Rating		57	40	49	46
		50		45	
Minutes to 25" Hg. ΔP		>300	142	273	222
		298		204	
ΔP ins. Hg. at 300 Minutes		8.37	>25	>25	>25
		>25		>25	

*Composition:
K28A - Mid-Continent Kero + Alkylate after 26 wks. storage at 110 F
K28AH - K28A Hydrotreated
K29A - Gulf Coast Kero + Alkylate after 26 wks. storage at 110 F
K29AH - K29A Hydrotreated
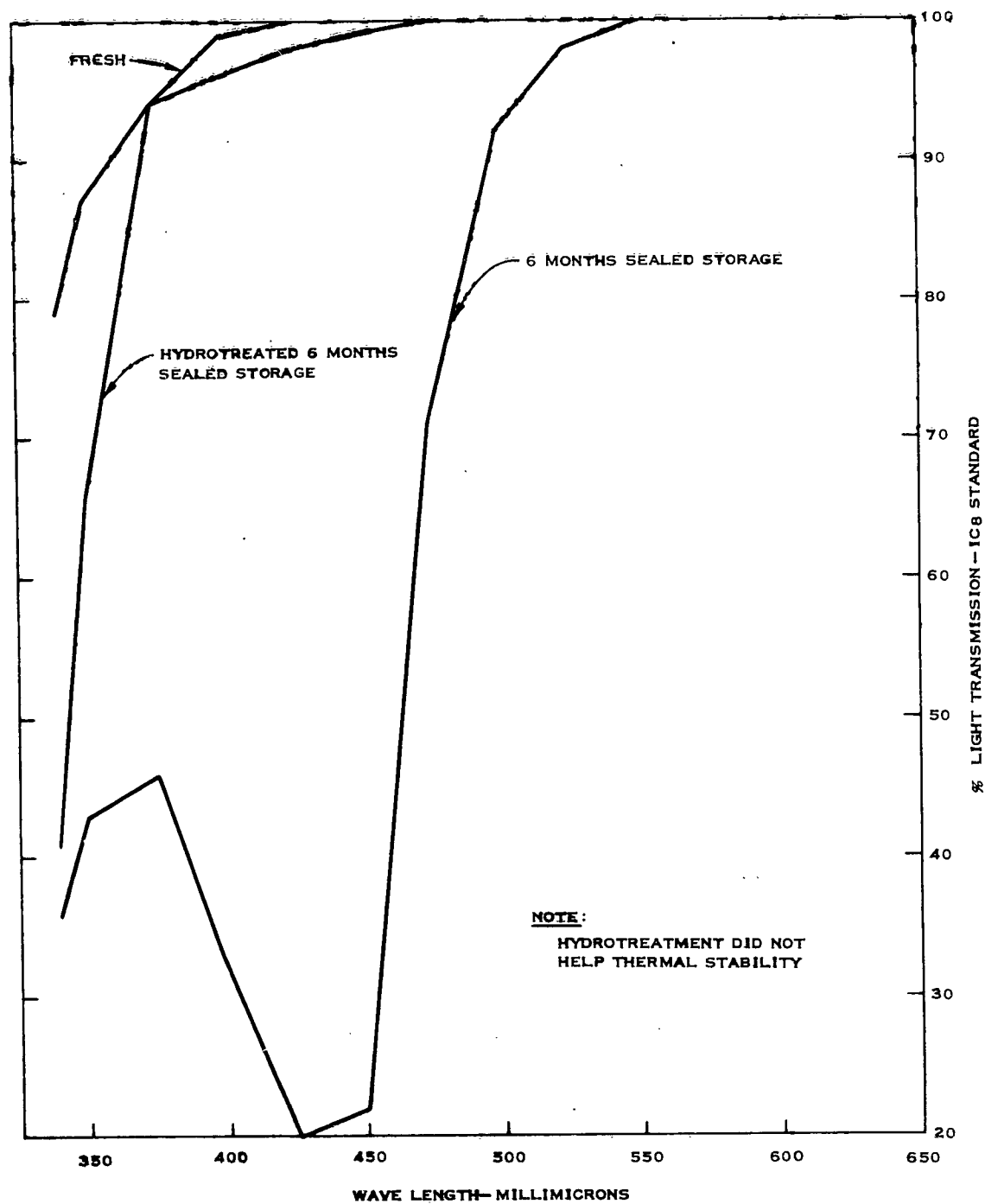
**At test conditions of 400 F/500 F/6 pph

FIGURE 46
LIGHT TRANSMISSION THROUGH JP-6 JET FUELS

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GULF COAST KERO. + ALKYLATE (K29)

FRESH

6 MONTHS SEALED STORAGE

HYDROTREATED 6 MONTHS
SEALED STORAGE

NOTE:

HYDROTREATMENT DID NOT
HELP THERMAL STABILITY

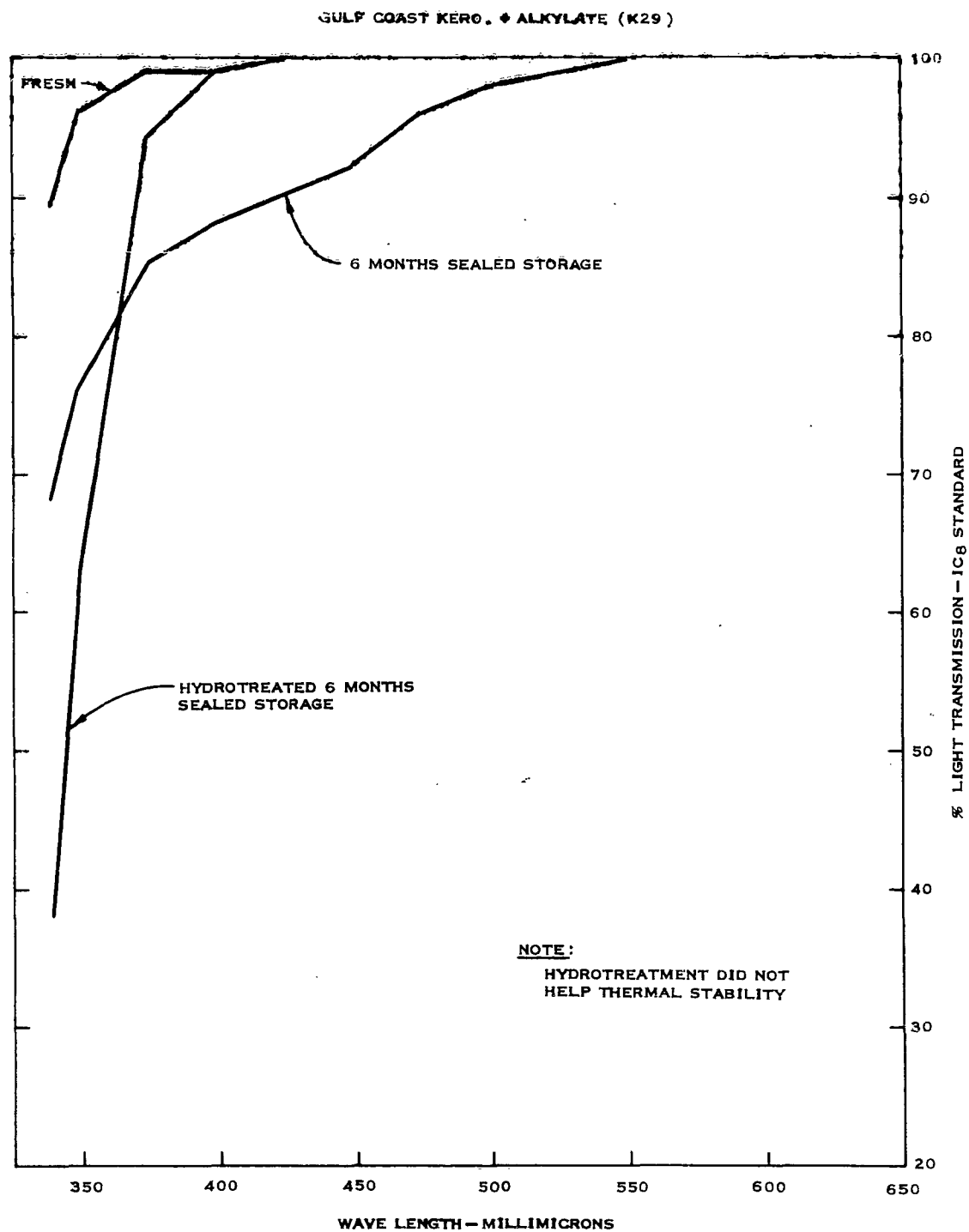% LIGHT TRANSMISSION – IC₈ STANDARD

WAVE LENGTH – MILLIMICRONS

FIGURE 47
LIGHT TRANSMISSION THROUGH JP–6 JET FUELS

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TABLE XI

PHYSICAL AND CHEMICAL ANALYSIS DATA ON JP-6 ADDITIVE JET FUELS BEFORE AND AFTER 110 F STORAGE

Fuel Ident.:* BJ60-10-		K500 Fresh	K500 26 Wks. Vented 110 F Storage	K31 Fresh	K31 26 Wks. Vented 110 F Storage	K32 Fresh	K32 26 Wks. Vented 110 F Storage	K33 Fresh	K33 26 Wks. Vented 110 F Storage	K34 Fresh	K34 26 Wks. Vented 110 F Storage	K35 Fresh	K35 26 Wks. Vented 110 F Storage	K29 26 Wks. Vented 110 F Storage	K53** 26 Wks. Vented 110 F Storage
Distillation: D86	IBP	320	318	320	322	318	322	317	321	322	318	324	321	314	318
	10%	332	335	338	334	334	335	338	335	334	333	336	335	392	336
	50	366	364	368	364	366	364	368	364	364	362	364	365	379	379
	90	458	456	460	460	454	458	462	456	457	454	463	457	450	448
	EP	516	514	518	512	512	516	522	514	514	512	520	518	476	480
	Recy.	99	99	99	99	98	99	99	99	99	98.5	99	98.5	99	99
	Res.	1	1	1	1	2	1	1	1	1	1.5	2	1.5	1	1
API Gravity @ 60 F		50.4	50.4	50.2	50.2	50.2	50.1	50.1	50.4	50.1	50.2	50.3	50.4	49.1	49.4
Steam Jet Gum, 450 F mg/100 ml		0.5	0.3	0.5	0.3	0.9	9.4	0.6	0.1	0.0	1.1	0.0	0.2	0.4	0.0
16 Hr. Steam Jet Gum, 450 F mg/100 ml.		0.6	—	0.6	—	1.3	—	3.1	—	1.8	—	0.6	—	—	—
Corrosion		1	1	1	1	1	1b	1	1	1	1	1	1	1b	1
Water Reaction		+30	+28	+30	+26	+28	+17	+28	+27	+23	+14	+16	+15	+6	Pink
Saybolt Color: Fresh		+30	+2C	+26	+23	+28	+17	+26	+13	+22	+16	-2	+13	+4	Pink
After Filtering		—	+15	—	+19	—	-9	—	-5	-2	-2	-14	+3	+23	.05
After Test		—	—	0.0	0.0	0.0	0.05	-9	0.05	0.02	0.00	0.0	0.0	0.03	
Neutralization No.		—	0.05	0.9	—	7.5	4.32	1.0	—	1.3	—	0.62	—	1.61	
Basic Nitrogen: Before Test	ppm	0.9	1.41	0.7	—	6.2	2.26	0.7	—	1.2	—	0.62	—	1.44	0.5
After Test	ppm	0.7	1.1	2.2	0.6	0.5	>518.6	0.2	0.3	0.6	<1.0	0.3	0.51	1.2	6.5
Peroxides: Before Test	ppm	—	0.4	13.1	2.3	32.0	249.3	1.7	2.9	1.7	1.2	3.1	1.2	14.6	0.042
After Test	ppm	—	7.3	0.068	0.12	0.063	0.23	0.032	—	0.06	—	0.03	—	0.02	
Oxygen: Before Test	Wt. %	—	0.075	0.050	—	0.11	0.18	—	—	—	—	0.042	—	0.05	
After Test (Chromatographic)	Wt. %	—	—	0.86	—	—	—	—	—	—	—	—	—	0.29	
Bromine No.: Before Test		—	0.61	0.54	—	—	—	—	—	—	—	—	—	0.30	
After Test		—	0.56	—	—	—	—	—	—	—	—	—	—		

* Composition:
  K500 = 60 wt. % West Texas Kero. + 15 Wt. % 350-550 F Alk. + 25 Wt. % 290-390 F Alk.
  K31 = K500 + 0.05 Wt. % 2,6-di-tert-butyl-4-methyl phenol.
  K32 = K500 + 0.01 Wt. % Mixed C₁₂-C₁₄ tert-alkyl primary amines.
  K33 = K500 + 0.01 Wt. % experimental hindered phenol
  K34 = K500 + 0.05 Wt. % 2,2' methylene-bis-(4-methyl-6-tert-butyl phenol).
  K35 = K500 + 0.10 Wt. % 4,4' methylene-bis-(2,6-di-tert-butyl phenol).

** - K29 stored for 26 wks. in vented drum coated inside with EC776SR

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gum content. Both blends K34 and K35 containing the bisphenol type antioxidants showed immediate darkening in color -- however, though the former darkened further during storage the latter remained unchanged, which parallels their relative change in thermal stability rating. Fuel K29 when stored in the sealant coated drums turned pink in color -- which appeared to represent a dye picked up from the sealant having no significance with respect to thermal stability rating. The high basic nitrogen analyses for blend K32 containing the $C_{12}-C_{14}$ tert-alkyl primary amines apparently reflects the nitrogen in the additive itself.

Figures 48 through 53 show the detailed light transmission characteristics for the additive blends and for fuel K29 in the sealant-lined drums. Fuels K31 and 33, which changed only slightly in thermal stability quality in storage also showed little change in light transmission. Fuels K32 and K34 which did become poorer in thermal stability rating also changed measurably in light transmission -- particularly the former. Thus the pattern shown for the non-additive test fuels was matched by four of the additive blends. However, blend K35 does not fit the pattern. This fuel, which contained the only additive causing a large change in light transmission characteristics upon blending, also showed significantly reduced light transmission after storage while remaining unchanged in thermal stability rating.

This illustrates that the use of changes in optical characteristics as an index of jet fuel thermal stability characteristics can be misleading if the fuel contains additives which themselves influence light transmission through the complete fuel in the 350 millimicron wavelength range.

Interestingly enough however, Figure 53 shows that the fuel sample stored in drums coated with MMM-EC776SR, which turned pink as shown by the strong light absorption through the 450-600 millimicron range, still had the same absorption characteristics as the sample stored in uncoated drums at wavelengths below 400 millimicrons -- matching their respective thermal stability performance.

Table XII lists additional laboratory data on the complete group of fuels (vented samples only) for intermediate periods of 8 and 16 weeks, supplementing the complete 26 weeks data discussed in the foregoing. These data serve mainly to reinforce the evidence of Saybolt color changes with the least storage stable fuels. It is also apparent that a consistent drop in water content occurred during storage, which is perhaps due either to "stripping" during the periodic aeration of the samples or to dropping out of solution. It may be recalled that all the vented samples were water saturated prior to storage though this, as with air saturation, appeared to have no effect measurable on subsequent thermal stability performance. Peroxide concentration did not change particularly with storage except for fuel K32 containing the amine-type antioxidant.

Thus, to date the chemical analysis results have not identified the specific reactants in fuels K27, 28 and 29 which altered in storage in such a way as to cause poorer thermal stability performance. The potential influence of solids contamination on such storage changes was, of course, demonstrated with one of the storage drums containing fuel K30. The most apparent common denominators in the composition of the three fuels which deteriorated in storage were as follows: - (1) sulfur contents were slightly higher than the other two fuels,

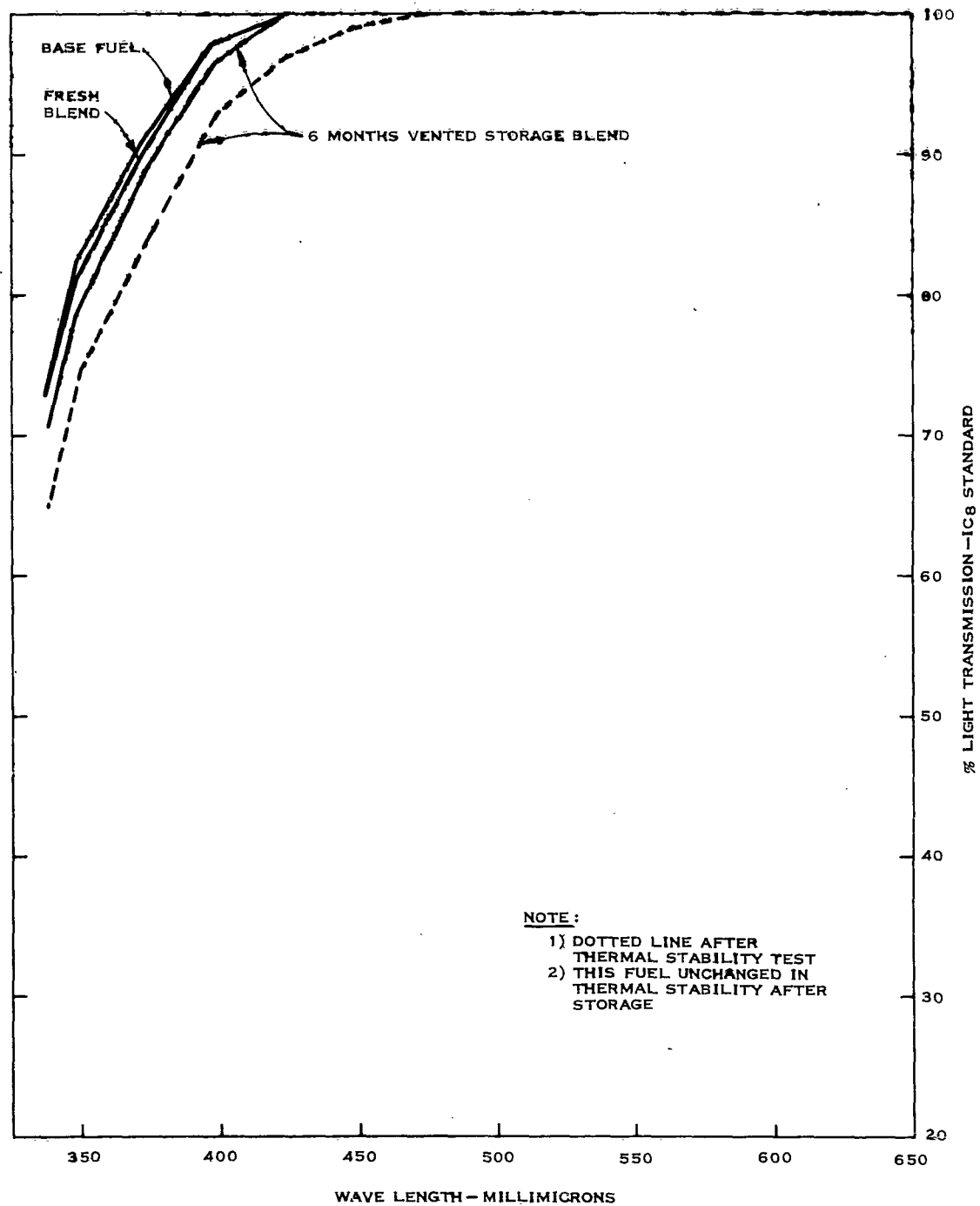K500 + 0.05 WT. % 2,6-DITERT.-BUTYL- 4-METHYL PHENOL (K31)
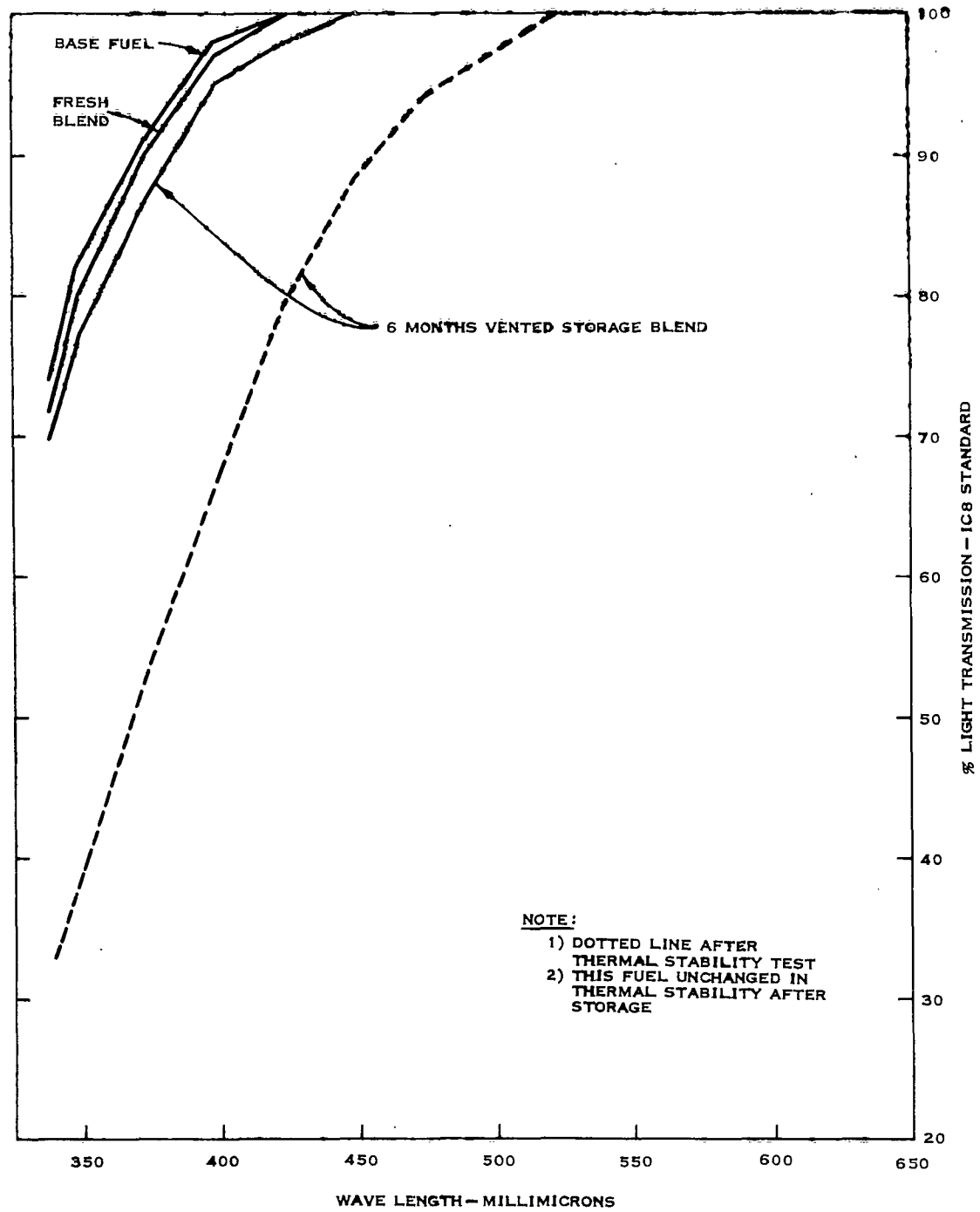

FIGURE 48
LIGHT TRANSMISSION THROUGH JP-6 JET FUELS

FIGURE 50
LIGHT TRANSMISSION THROUGH JP-6 JET FUELS

K500 +0.05 WT.% 2,2' METHYLENE-BIS(4-METHYL-6 TERT.-BUTYL PHENOL) (K34)
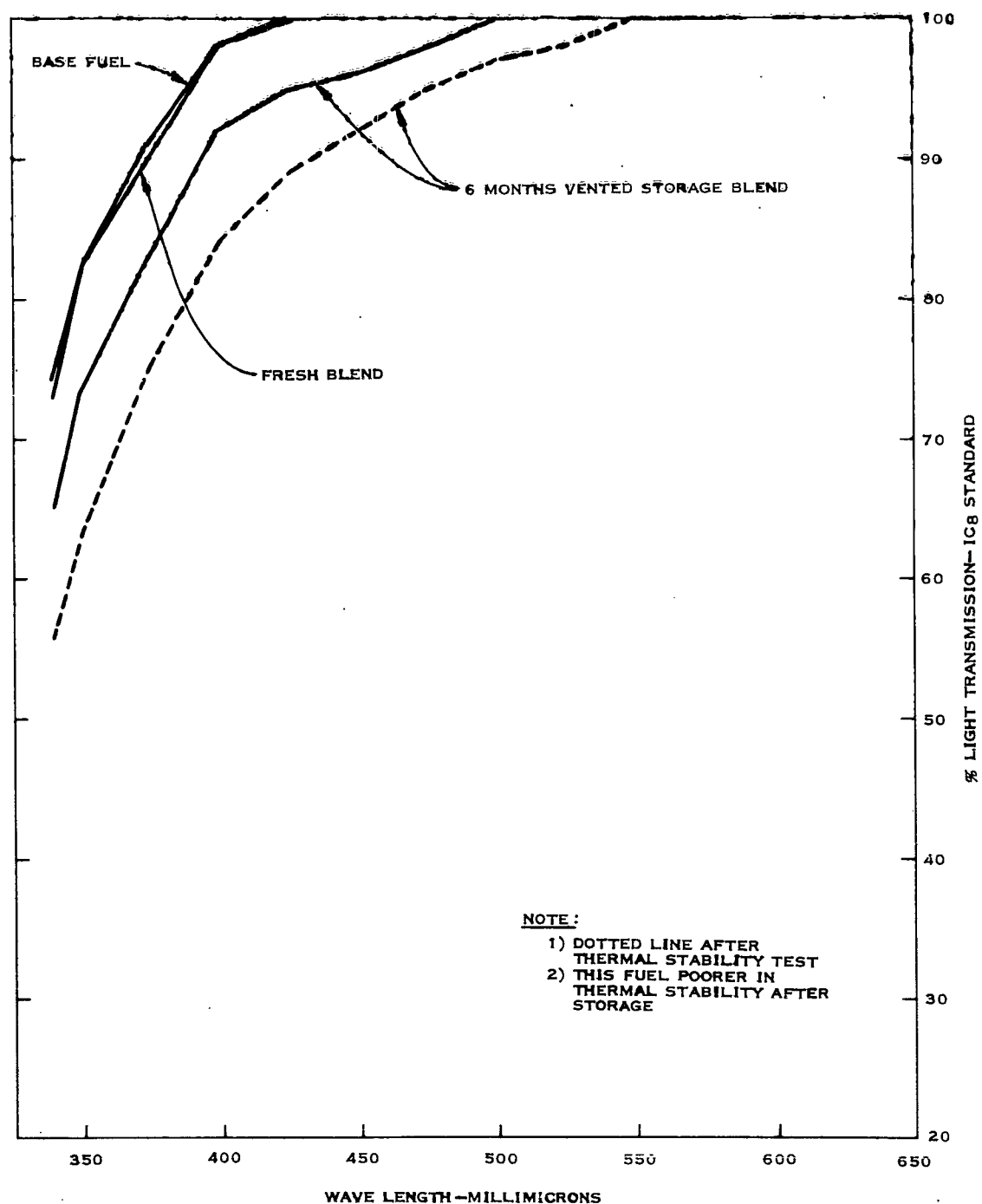

FIGURE 51
LIGHT TRANSMISSION THROUGH JP-6 JET FUELS

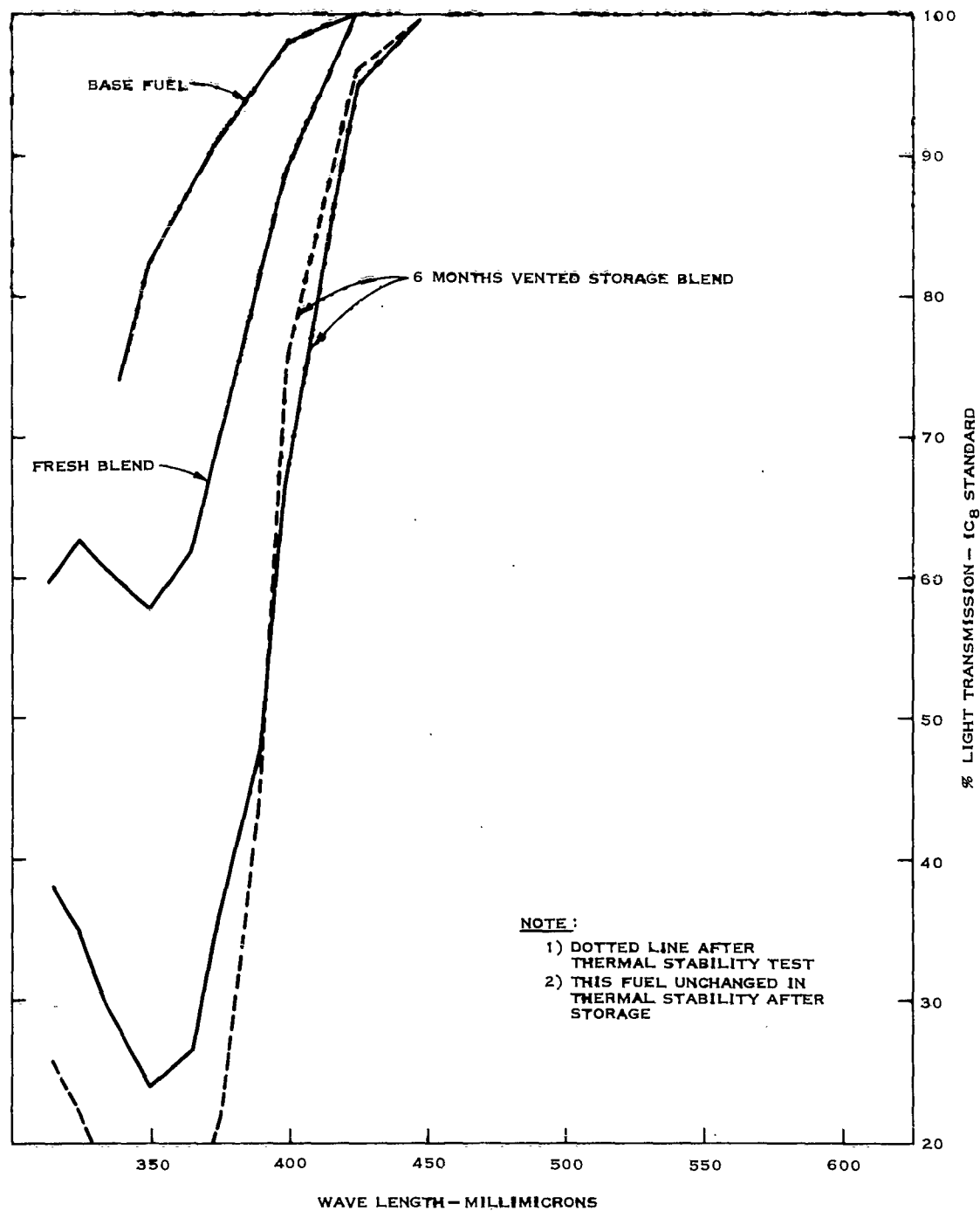K500 ♦ 0.10 WT. % 4,4' METHYLENE BIS(2,6-DITER.-BUTYL PHENOL) (K35)

FIGURE 52
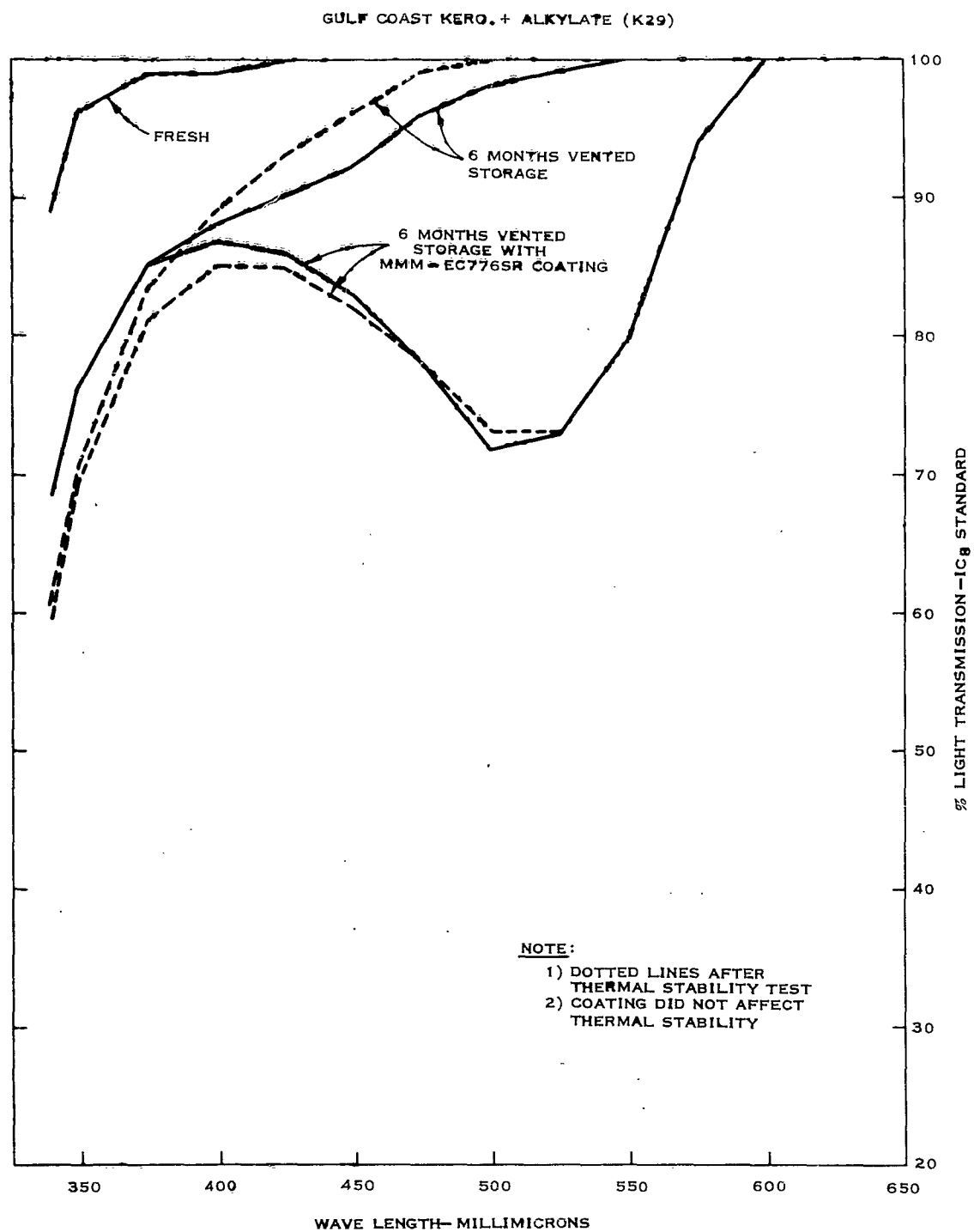LIGHT TRANSMISSION THROUGH JP-6 JET FUELS

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GULF COAST KERO. + ALKYLATE (K29)

FIGURE 53
LIGHT TRANSMISSION THROUGH JP−6 JET FUELS

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TABLE XII

SELECTED CHEMICAL ANALYSIS DATA ON JP-6 FUELS FOR INTERIM PERIODS

Fuel Ident: BJ60-10-	K26	K27	K28	K29	K53	K30	K500	K31	K32	K33	K34	K35
Water Content, ppm												
Fresh	30	40	32	45	--	28	--	--	--	--	--	--
After 8 Wks, Vented	56	128	89	95	125	130	116	129	117	120	41	44
After 16 Wks, Vented	53	56	55	44	48	31	37	41	109	57	7	9
After 26 Wks, Vented	11	26	6	<5	16	37	--	14	194	--	--	--
After 26 Wks, Sealed	25	21	33	68	--	29	--	--	--	--	--	--
Saybolt Color												
Fresh	+30	+17	+20	+30	--	+24	+30	+30	+28	+28	+23	+16
After 8 Wks, Vented	+18	+10	+16	+12	Pink	+20	+23	+26	+20	+23	+19	+20
After 16 Wks, Vented	+18	+16	-15	+16	Pink	+22	+23	+26	+18	+20	+15	+16
After 26 Wks, Vented	+22	+13	Too	+6	Pink	+20	+28	+26	+17	+27	+14	+15
After 26 Wks, Sealed	+26	+13	Dark	+4	Pink	+22	--	--	--	--	--	--
Neut. No.												
Fresh	.00	.04	.04	.04	--	.04	--	.00	.00	.00	0.02	.00
After 8 Wks, Vented	.10	.00	.03	.03	.01	.04	.00	.01	.00	.00	.12	.32
After 16 Wks, Vented	.23	.00	.01	.02	.12	.23	.14	.10	.20	.20	.01	.00
After 26 Wks, Vented	.22	.02	.02	.01	.05	.02	--	.00	.05	--	.00	.00
After 26 Wks, Sealed	.20	.03	.04	.02	--	.00	--	--	--	--	--	--
Basic Nitrogen, ppm												
Fresh	4.8	4.0	<1.0	1.0	--	1.5	--	0.9	7.5	1.0	1.3	.62
After Coker Test	3.0	3.0	<1.0	1.5	--	0.6	--	0.7	6.2	0.7	1.2	.62
After 8 Wks, Vented	3.6	4.1	1.03	1.3	2.3	1.24	1.22	1.25	7.4	1.04	1.4	1.16
After 16 Wks, Vented	2.22	3.9	1.3	1.5	1.78	1.34	1.0	0.99	5.8	1.0	1.24	1.36
After 26 Wks, Vented	3.1	2.9	.99	1.61	--	.87	--	--	4.32	--	--	--
After Coker Test	2.7	3.02	.62	1.44	--	.95	--	--	2.26	--	--	--
After 26 Wks, Sealed	3.6	3.6	1.69	1.70	--	.87	--	--	--	--	--	--
After Coker Test	2.8	3.06	1.16	1.44	--	.95	--	--	--	--	--	--
Peroxides, ppm												
Fresh	.5	1.1	1.6	1.9	--	7.7	--	2.2	.5	.2	.6	.3
After Coker Test	9.6	15.1	9.4	1.1	--	4.5	--	13.3	32.0	1.7	1.7	3.1
After 8 Wks, Vented	.5	1.24	1.14	1.2	.31	.39	.2	9.2	1.45	.39	.42	.48
After 16 Wks, Vented	1.76	.10	1.27	.64	.63	1.14	1.5	.83	>166.5	.19	.44	4.05
After 26 Wks, Vented	1.12	.19	1.8	1.2	.5	10.1	.4	.6	>518.0	.3	<1.0	.51
After Coker Test	20.00	9.4	6.6	14.6	6.5	12.2	7.3	2.3	259.3	2.9	1.2	1.2
After 26 Wks, Sealed	<.1	.49	1.3	1.2	--	4.1	--	--	--	--	--	--
After Coker Test	10.5	7.4	5.8	10.7	--	9.8	--	--	--	--	--	--

K26 - WADD Sample F-60-5, K27 - WADD Sample F-60-3
K28 - Mid Continent Kerosine + Alkylate Blend
K29 - Gulf Coast Kerosine + Alkylate Blend
K53 - K29 Blend stored in drums coated with MMM-EC7776SR
K30 - West Texas Kerosine + Alkylates
K500 - Reblend of K30
K31 - K500 + .05 Wt.% 2,6-di-tert-butyl-4-methyl phenol
K32 - K500 + .01 Wt.% mixed C_{12}-C_{14} tertiary Alkyl Primary Amines
K33 - K500 + .01 Wt.% experimental hindered phenol
K34 - K500 + .05 Wt.% methylene-bis-4-methyl-6-tertiary butyl phenol)
K35 - K500 + .10 Wt.% 4,4'-methylene-bis-(2,6-di-tert-butyl phenol)

(2) all three contained 1 to 3 per cent by weight of polycyclic aromatics
(3) one of the three contained appreciably higher concentrations of soluble copper than the other fuels.

A possible influence of contamination by lead on fuel thermal stability was indicated for two fuels otherwise identical in composition but differing significantly in CFR Fuel Coker rating at 400 F temperature.

The consistent light transmission changes with fuels which deteriorated in thermal stability following storage suggests the selective oxidation of fuel constituents of condensed molecular structures and future chemical analysis work will attempt to establish this.

C. Supplementary Experiments

This section summarizes a series of CFR Fuel Coker tests carried out on blends of various pure compounds in base fuels of known thermal stability characteristics, to help point out potential classes of fuel components contributing to the thermal stability problem at 400 F-plus temperatures and aid interpretation of the six months 110 F hot room storage results.

In an earlier section of this report a series of tests with a small scale recirculating thermal stability tester was discussed which indicated that, with one JP-6 fuel blend, the deposit-forming components were identified with the 400 F-plus boiling range fraction. Gas chromatography analyses suggested that polycyclic aromatic hydrocarbons might be potential deposit precursors under these conditions. Therefore, CFR Fuel Coker tests were carried out with experimental fuel blends with naphthalene concentration as a controlled variable. The base fuel used for these experiments was a 350-550 F boiling range alkylate (isoparaffinic) fraction containing no aromatics or non-hydrocarbon impurities to speak of, and rating extremely high in CFR Fuel Coker thermal stability performance. Table XIII lists some of the pertinent physical and chemical characteristics of this product. The addition of only 1.0 weight per cent of alpha methyl naphthalene was found to produce a striking deterioration in CFR Fuel Coker rating, which led to tests with a variety of other aromatic compounds and potential naphthalene oxidation products. These data are listed in Table XIV and presented graphically in Figure 54. The AMN used was fairly fresh ASTM grade material as supplied for reference fuel purposes for knock rating of diesel fuels. Nevertheless it is known to be of uncertain uniformity as to actual proportions of AMN present as opposed to other naphthalenes. Therefore, the test was repeated using a redistilled sample of AMN in which the front 10 per cent and 20 per cent bottoms fraction were discarded to eliminate aromatics other than methyl naphthalenes and any extraneous naphthalene oxidation products as well. Though this would not have eliminated beta methyl naphthalene, this distinction is of no particular importance for the present work where the effects of naphthalenes as a class was the main interest (at this point). The redistilled material had an equally potent adverse effect on CFR Fuel Coker rating. A third test was carried out using the redistilled AMN in which oil-free nitrogen gas was bubbled through the test fuel sample for one hour prior to the test and throughout the entire five hours duration of the test itself, thus excluding oxygen as completely as possible from contact with the fuel stream entering the CFR Fuel Coker hot section. Results of this test showed markedly better

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TABLE XIII

TYPICAL PROPERTIES OF ISOPARAFFINIC ALKYLATE FRACTION* USED

AS BASE FUEL FOR PURE HYDROCARBON BLENDS

Steam Jet Existent Gum, mg/100 ml	0.6
Potential Gum, Total, mg/100 ml	3.3
Solubles	-
Insolubles	-
ASTM Distillation	
IBP, F	362
10% Evaporated	372
50% Evaporated	395
90% Evaporated	487
EP	570
API Gravity, degrees	53.0
Composition, vol. %	Essentially 100% Paraffins
Flash Point, F	142
Net Heat of Combustion, Btu/lb.	18,923
Sulfur Content, % Wt.	
Total	0.005
Mercaptans	<0.001

*Phillips Base Oil #1

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TABLE XIV

THERMAL STABILITY RATINGS OF SYNTHETIC BLENDS

	Test Temp. °F Preheater	Filter	Tube Ratings 0	1	2	3	4	5	6	7	Max. Rating	Filter Merit Rating	Minutes to 25" Hg ΔP	ΔP" Hg at 300 Minutes
1. 350-550 F Isoparaffinic Fuel (B46)	450	550	13	0	0	0	0	0	0	0	0	99	>300	0.00
2. (1) + 1.0 Vol. % ASTM Grade AMN(a) (J70)	450	550	6	0	1	0	2	2	2	0	6	46	223	>25.00
3. (1) + 1.0 Vol. % redistilled AMN(a) (J72)	450	550	5	1	1	0	1	2	3	0	6	50	300	25.00
4. (3) N2 purged and blanketed (J73)	450	550	7	1	2	3	0	0	0	0	3	67	>300	1.54
5. (1) + 0.45 Vol. % 95 purity AMN(a) (K91)	450	550	7	6	0	0	0	0	0	0	1	72	>300	0.78
6. (1) + 0.45 Vol. % ASTM Grade AMN(a) (K92)	450	550	5	1	0	1	5	1	0	0	5	66	>300	2.10
7. (1) + 0.45 Vol. % redistilled AMN(a)(K90)	450	550	7	0	1	1	2	2	0	0	5	77	>300	0.35
8. (1) + 0.25 Vol. % redistilled AMN(a)(K87)	450	550	9	1	2	1	0	0	0	0	3	76	>300	0.37
9. (1) + 1.0 Wt. % pure Naphthalene(b) (K78)	450	550	9	4	0	0	0	0	0	0	1	83	>300	0.13
10. (1) + 1.0 Vol. % triethyl benzene(e) (K71)	450	550	13	0	0	0	0	0	0	0	0	99	>300	0.02
11. (1) + 1.0 Vol. % phenyl butene-2 (d) (K79)	450	550	13	0	0	0	0	0	0	0	0	75	>300	0.49
12. (1) + 1.0 Vol. % n-butyl benzene(e) (K80)	450	550	12	1	0	0	0	0	0	0	1	89	>300	0.05
13. (1) + 1.0 Vol. % pure Cumene(f) (K81)	450	550	13	0	0	0	0	0	0	0	0	99	>300	0.02
14. (1) + 1.0 Vol. % tetralin(g) (K85)	450	550	10	3	0	0	0	0	0	0	1	79	>300	0.24
15. (1) + 0.25 Vol. % redistilled Indene(h) (K89)	450	550	7	3	1	2	0	0	0	0	3	86	>300	1.09
16. (1) + 0.25 Wt. % 1-Naphthol(i) (K82)	450	550	6	2	1	0	1	2	1	0	6	40	.138	>25.00
17. (1) + 0.10 Wt. % 1,4-naphthoquinone(j) (K95)	450	550	10	2	1	0	0	0	0	0	2	99	>300	0.02
18. (1) + 0.10 Wt. % 2-Naphthol(k) (K96)	450	550	9	0	1	0	1	0	2	0	6	44	189	>25.00
19. JP-6 blend Gulf Coast Kerosine (B66)	450 / 450	550 / 550	7 / 6	0 / 0	2 / 0	0 / 1	1 / 1	2 / 2	1 / 3	0 / 0	6 / 6	38 / 35	117 / 95	>25.00 / >25.00
20. (19) N2 purged (K68)	450	550	6	0	0	1	1	1	1	3	7	47	235	>25.00
21. (19) N2 purged and blanketed (K68)	450 / 450	550 / 550	6 / 6	2 / 1	1 / 0	2 / 2	2 / 2	0 / 1	0 / 2	0 / 0	4 / 6	99 / 99	>300 / >300	0.00 / 0.00
22. JP-6 Blend Gulf Coast Kerosine (K74)	400	500	9	2	2	0	0	0	0	0	2	61	>300	4.13
23. (22) + 0.023 Vol. % Mixed Naphthenic Acids(1)(K75)	400	500	9	4	0	0	0	0	0	0	1	89	>300	0.05
24. (22) + 0.23 Vol. % Naphthenic Acids(1) (K76)	400	500	13	0	0	0	0	0	0	0	0	99	>300	0.00

(a) Reilly ASTM Grade
(b) Fisher Pure Naphthalene
(c) Dow Alkazene-3
(d) Phillips Technical Grade
(e) Phillips Pure Grade
(f) Phillips Pure Grade

(g) Fisher Purified
(h) Matheson Technical Grade
(i) Eastman (170)
(j) Eastman Practical Grade
(k) Eastman (171)
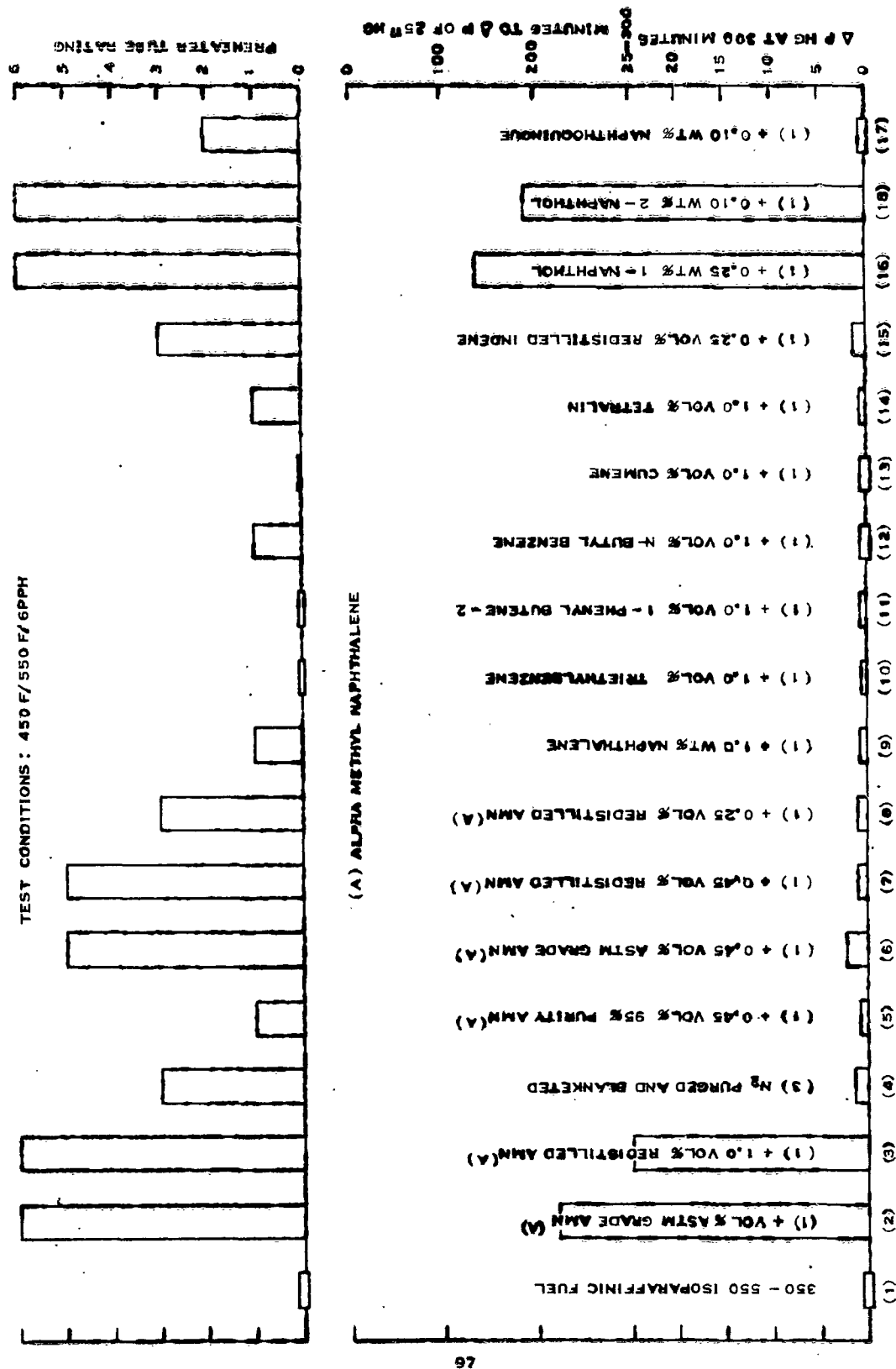(l) Eastman Practical Grade

FIGURE 54

CFR FUEL COKER RATINGS OF EXPERIMENTAL FUEL BLENDS

TEST CONDITIONS : 450 F/ 550 F/ 6PPH

(A) ALPHA METHYL NAPHTHALENE

performance than when normal pre-aeration of the fuel was employed, suggesting that oxidation is an important step in the reactions participated in by the contaminant. Although the performance remained somewhat poorer than paraffinic base fuel alone, it is not known quantitatively how much of the oxygen originally dissolved in the test fuel sample was successfully "stripped" away by the nitrogen-purging process. Additional tests were then carried out at lower concentrations with both the complete and the redistilled ASTM grade AMN, and with a single sample (available in very small quantity) of a 95 per cent purity AMN batch. The adverse effects of the latter material were very much less than either the redistilled or "as-is" ASTM AMN, though still measurable. A sample of pure naphthalene tested in 1.0 weight per cent concentration in the base oil showed no significant adverse effect on thermal stability performance at these temperature conditions.

Therefore, chemical analyses were made to establish the nature and amount of impurities present in the batch of ASTM grade AMN used for the CFR Fuel Coker tests showing the strongest adverse effects. Results were as follows:

Component		ASTM-AMN	70% Heart Cut ASTM-AMN
Alpha-methyl-naphthalene ⎫	gas	61 Wt. %	58 Wt. %
beta-methyl naphthalene ⎬ chromatography		35	37
heavier ⎭		4	5
Total Sulfur, X-ray fluorescence		0.82	0.80
Oxygenated compounds, infrared		Strong "OH" bands	Strong "OH" bands

It is shown that contaminants in addition to other naphthalene hydrocarbons were definitely present in both the original and redistilled samples of this product. Further attempts to identify the material termed "heavier" in the gas chromatography analysis indicated that it is probably associated with the "OH" band absorption shown by the infrared spectra. The fact that this material apparently boils within a degree or two of the methyl naphthalenes would appear to rule out methylnaphthalene oxidation products or even naphthols, unless an azeotrope exists. Mass spectrometry showed this unknown to have a mass number which could be accounted for by a tetrahydronaphthol structure. Since both the original and redistilled AMN samples showed 0.8 per cent by weight of sulfur contaminant, another possibility would be heterocyclic compounds containing a sulfur atom in the ring and a hydroxyl group attached.

In any event it was established that these ASTM grade AMN samples did contain appreciable non-naphthalenic contaminants which therefore clouds the effects observed on thermal stability. The 95 per cent purity alphamethylnaphthalene was examined by infrared and showed no hydroxyl bonds, betamethylnaphthalene in very minor quantities being the only contaminant.

Further, CFR Fuel Coker testing was carried out with four different benzene nucleus aromatic compounds blended to 1.0 per cent concentration in this base fuel, including one (phenyl butene-2) with an olefinic side chain and another (isopropyl benzene) with which considerable data are available as to liquid phase oxidation characteristics. None of these showed significant effects on thermal stability performance. A test with tetralin as the contaminant showed similar lack of response

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-- and tetralin is another hydrocarbon whose tendency towards slow oxidation in the liquid phase is well known. A sample of redistilled indene did show adverse effects on stability performance - however subsequent infrared analysis showed appreciable carbonyl absorption in the indene.

Thus, in every instance in which the addition of an aromatic hydrocarbon to the base fuel caused significantly poorer performance in the CFR Fuel Coker, oxidized impurities were present. Therefore, to check the direct effects of potential hydrocarbon oxidation products, tests were carried out in which small concentrations of 1 and 2 naphthol were added to the base fuel. In both cases (see Figure 54) very potent adverse effects were observed. However, a third compound, 1,4-naphthoquinone showed only questionable adverse effects.

More work along these lines is planned, however at this stage it can be said only that (1) a strong adverse effect of certain aromatic oxidation products on CFR Fuel Coker rating at 450-550 F was shown and (2) an adverse effect of the aromatics themselves during short term exposure to high temperatures in the CFR Fuel Coker has not been shown.

As to the effects of oxygen availability on thermal stability performance, further work was done with a different test fuel, a reblended batch of one of the JP-6 storage fuels (Gulf Coast kerosine plus alkylate-K29) containing 2.9 weight per cent polycyclic aromatics by UV analysis. A CFR Fuel Coker rating at 450-550 F temperature conditions using the normal preaeration procedure rates this test fuel as a positive "fail" by both filter plugging and heater deposition criteria. Substitution of one hour nitrogen purging for aeration produced only a slight improvement in rating if the vented run tank was allowed to draw in air as the fuel level dropped, which is normally the case. If the nitrogen bubbling was continued throughout the Coker test, however, to maintain a nitrogen blanket above the fuel level and prevent air intake, the rating was much better, as with the previously discussed synthetic naphthalene blend. Figure 55 shows these trends graphically.

A possible implication of this is that preparation and storage, under inert atmospheres, of high thermal stability jet fuels might not have the desired beneficial effects on thermal stability performance in the jet power plants if the fuel tanks in the aircraft itself were not also inerted.

Analyses for peroxide level were made before and after thermal stability testing of the aerated and completely inerted samples of this test fuel, and are listed below.

Fuel	Condition Prior To CFR Coker Test	Peroxide No., Millequivalents, Active O_2 per Liter	
		Before Test	After Test
JP-6 prepared from	Normal pre-aeration	0.06	0.67
Gulf Coast Kerosine	nitrogen purged + blanketed	0.08	0.14
plus alkylate			

These results agree with the trends shown by the CFR Coker tests themselves, in that much less peroxidation took place in the sample from which oxygen was excluded as completely as possible.
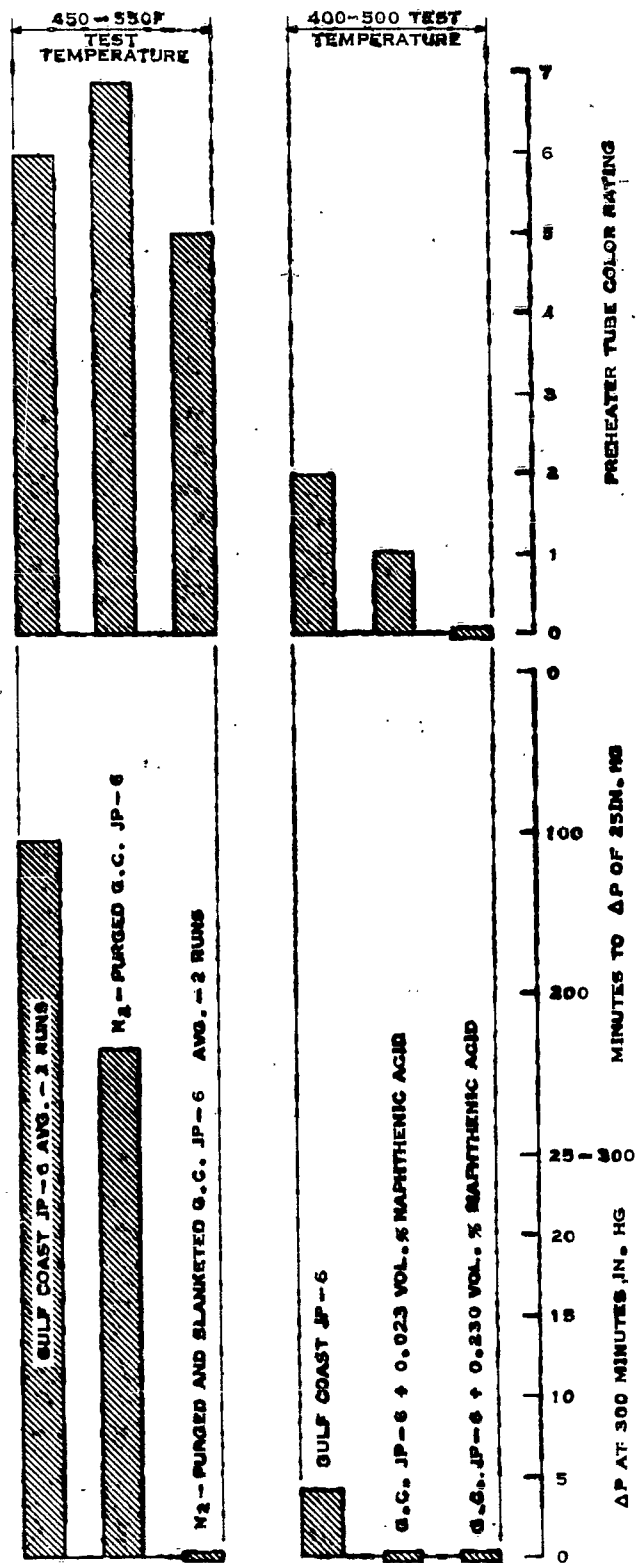
FIGURE 55

CFR FUEL COKER RATINGS OF EXPERIMENTAL FUEL BLENDS

Another type of oxygenated hydrocarbon which could conceivably be present in jet fuels which had not been caustic washed is represented by naphthenic acids, present in certain crude oils in very appreciable concentrations. At the request of WADD a short series of CFR Fuel Coker tests was carried out at 400-500 F temperature conditions using a second batch of the same JP-6 fuel employed for the preceding experiment, with naphthenic acid concentration as a controlled variable. Figure 55 shows the results of adding 0.023 and 0.230 vol. % of a mixed naphthenic acid fraction to this base fuel. It is apparent that thermal stability quality was not harmed and may actually have been helped.

In the previous section during the discussion of the storage results it was pointed out that with some of the fuels, deterioration in CFR Coker performance following storage was accompanied by increased light absorption characteristics in the 340-400 millimicron range of wavelengths. It was therefore considered of interest to evaluate the optical characteristics of some of the synthetic CFR Coker test blends with aromatic nucleus compounds, just discussed, from this standpoint.

Figures 56, 57 and 58 present these curves. Concerning the alphmethylnaphthalene blends, it is shown that an absorption peak around 390-400 millimicrons is present in all cases with blends containing the ASTM-AMN, either as-is or redistilled. This is not characteristic of methyl naphthalenes and therefore must accompany the presence of the impurity -- the 95 per cent Purity AMN did not show this absorption peak.

Concerning the general relationship between light transmission in the 350 millimicron wavelength range and thermal stability performance, this appears to hold in every case except for the 1,4-naphthoquinone, which had pronounced effects on light transmission with only slight adverse effects on thermal stability rating.

IV. CONCLUSIONS

A. Results of experimental development of small scale jet fuel thermal stability test methods during the first year of work under this contract were as follows:

   (1) A recirculating-flow type of test subjecting a one-liter fuel sample to alternating heating and cooling cycles was found to lay down hot section deposits whose effect on coefficient of heat transfer was measurable and consistent. Some agreement in trend existed between ratings in terms of coefficient of heat transfer after one hour of operation with JP-6 jet fuels and ratings at 400-500 F by the CFR Fuel Coker test.

   (2) Preliminary testing with a small scale static procedure employing an electrically heated nickel wire as both heat source and temperature sensing device has indicated that the rise in temperature of the wire as deposits accumulate from 250 ml fuel samples offers one possible approach to a very simple type of test to evaluate fuel thermal stability effects in a realistic manner.
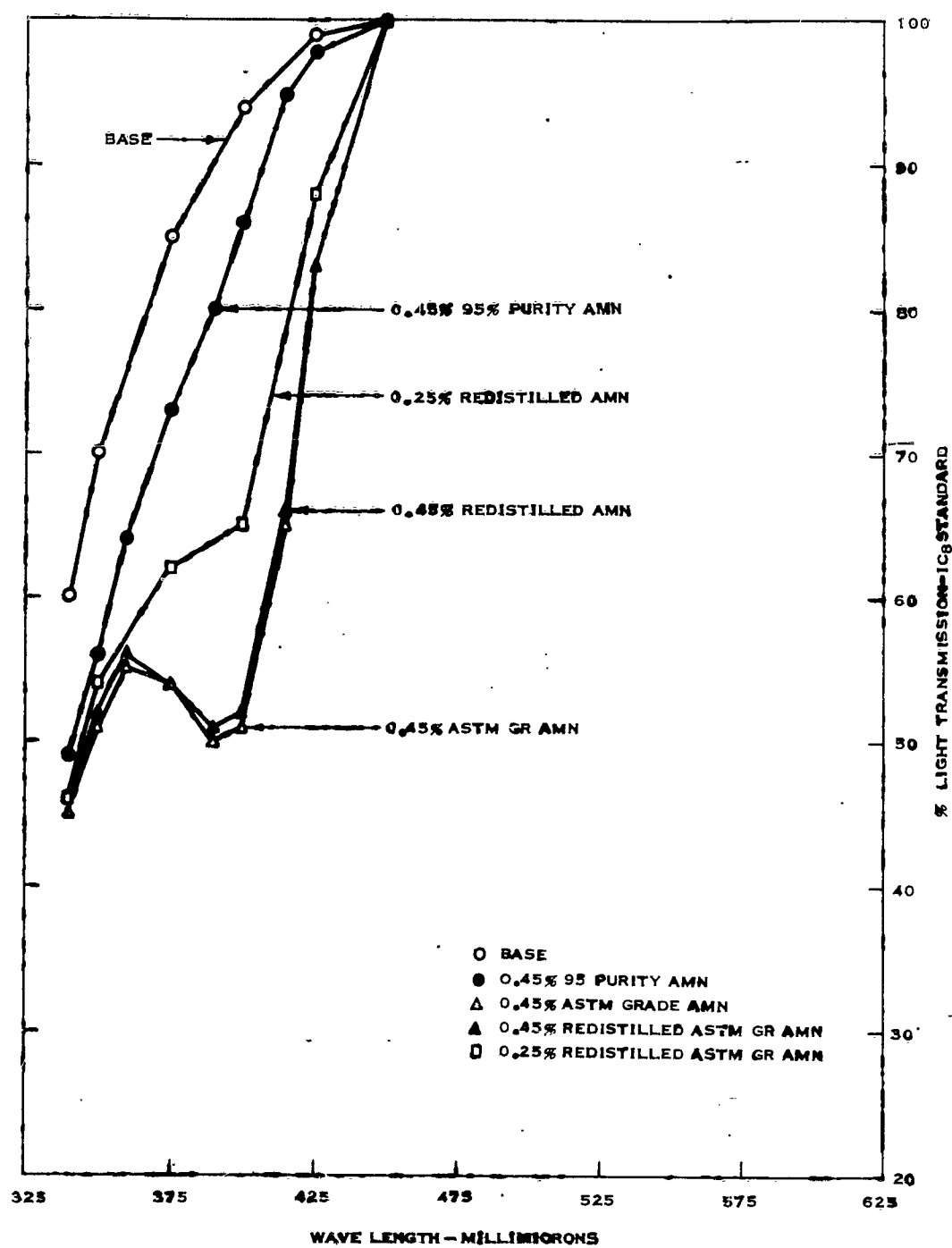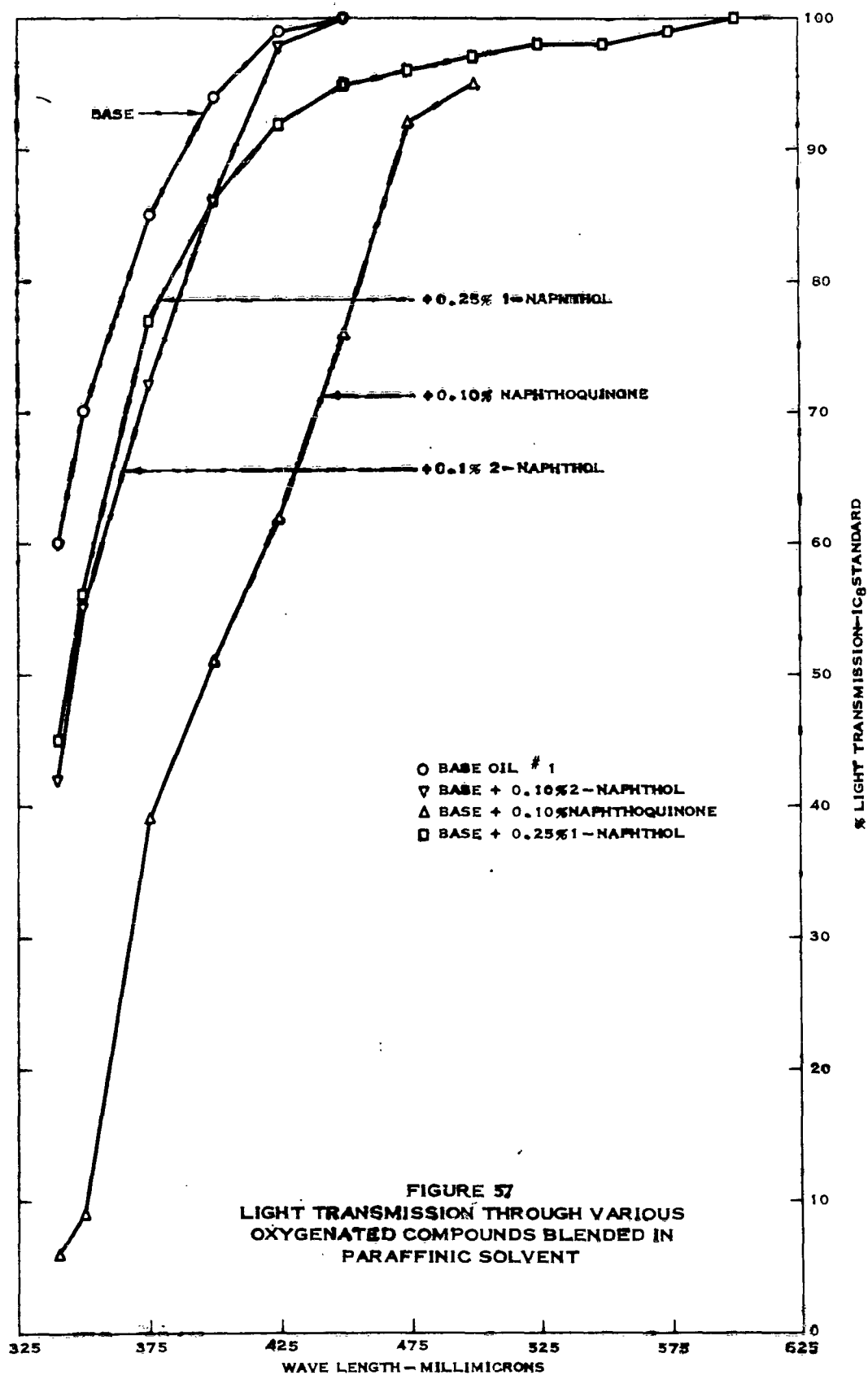
FIGURE 56
LIGHT TRANSMISSION THROUGH ALPHA METHYL
NAPHTHALENES BLENDED IN
PARAFFINIC SOLVENT

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FIGURE 57
LIGHT TRANSMISSION THROUGH VARIOUS
OXYGENATED COMPOUNDS BLENDED IN
PARAFFINIC SOLVENT

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(3) A very small scale (5 ml fuel sample) static thermal stability test was investigated using a small stainless steel bomb externally heated by radiation from a laboratory muffle furnace. An indirect empirical index of thermal stability was employed based on light transmission through the test fuels after heating to selected temperature levels. This technique appeared capable of separating fuels broadly into "good", "fair" and "poor" thermal stability categories.

B. Results throughout the first year of work on JP-6 jet fuel storage stability characteristics were as follows:

(1) Of five JP-6 fuels stored 26 weeks at 110 F with no additives present, one fuel did not change at all in terms of CFR Fuel Coker rating, a second fuel showed evidence of deterioration in only one storage drum (which was traced to build up in solids contamination), while the three remaining fuels deteriorated significantly in all storage drums.

(2) No significant differences in CFR Fuel Coker performance were observed between the vented samples of these test fuels after 26 weeks hot room storage and those sealed under a nitrogen atmosphere. Analyses showed 0.02-0.05 weight per cent oxygen present in fuels from both sealed and vented containers.

(3) The fuels which deteriorated in thermal stability after storage were relatively high in polycyclic aromatics, sulfur and (in one case) trace copper content.

(4) The only prominent chemical or physical change thus far identified which agrees in trend with the changes in thermal stability performance is darkening in color, which is most apparent in terms of light absorption at 340-400 millimicrons wavelength. This is presumed to reflect oxidation of certain fuel constituents of relatively condensed structures, but this has not yet been verified by analysis.

(5) Five blends of a poor thermal stability quality base fuel stabilized with commercial antioxidant additives showed one (containing 0.10 weight per cent bis-phenol rubber antioxidant) to be unchanged after storage, three (containing lower concentrations of other phenol-type additives) showing some evidence of deterioration and one (containing 0.01 weight per cent alkyl amines) badly deteriorated.

(6) A variety of pure aromatic compounds added in low concentrations to a very stable paraffinic base fuel caused strong adverse effects on thermal stability performance only with methyl naphthalene and indene samples containing oxidized impurities. Addition of two naphthol compounds also caused strong adverse effects on thermal stability, though a naphthoquinone and a mixed naphthenic acid fraction did not.

(7) The chemistry of high temperature deposit formation in the CFR Fuel Coker test was shown to involve oxidation by virtue of increases in peroxides content in all the fuels after testing plus marked improvement in performance when air was excluded from the test apparatus.

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V. FUTURE PLANS

Future efforts on the development of small scale jet fuel thermal stability test methods will be concentrated on the static hot wire and 5 ml bomb approaches, the recirculating flow type of test falling more within the scale of apparatus being studied under other Air Force contracts. At an early stage in the second year of work under this contract a decision will be made as to which of these two devices appears most promising, and the remainder of the period will be concentrated on the evaluation of fuels tested in other larger scale apparatus for correlation purposes.

Future plans for the JP-6 storage stability project include continuing efforts to explain by chemical analysis the changes in thermal stability of the fuels completing 26 weeks 110 F hot room storage during the period covered by the present report. In addition, the same group of fuels will complete 52 weeks of storage at ambient temperatures during this period, enabling comparison of these data with the hot room trends. Further chemical analysis work can then be done to pin down more conclusively which types of fuel constituents oxidized in storage to cause changes in performance, to allow recommending techniques for predicting and preventing such changes. To support these conclusions, several additional fuels will be stored for 26 weeks at 110 F in the hot room in the presence of known amounts of various fuel constituents or contaminants believed undesirable from this standpoint.

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May, 1961, 107 pp. with figs. and tables.
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(Contract AF 33(616)-7241)(Project 3048, Task
30178)(ASD TR 61-238)
                    Unclassified Report

One year of development work on small scale
thermal stability test methods for jet fuels
has produced three potentially useful tech-
niques, (1) a recirculating-flow dynamic
method measuring deposit insulating effects
around a heated surface requiring 1000 ml
fuel samples, (2) a static method measuring
deposit insulating effects around a heated

(over)

nickel wire requiring 150 ml fuel samples and (3) a static method based on changes in fuel light transmission characteristics after heating requiring 5 ml fuel sample. A JP-6 jet fuel storage stability investigation showed three out of five fuels significantly poorer after 26 wks. at 110F in terms of CFR Fuel Coker rating, while a fourth fuel showed evidence of deterioration in one container only which is attributed to solids contamination. Vented versus sealed-under-nitrogen storage had no influence on the changes. The only chemical or physical changes in the test fuel after storage which matched the thermal stability changes were the UV light transmission characteristics. The two fuels least affected by storage were low in both sulfur and polycyclic aromatics content.